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GROUNDWATER AND LEACHATE TREATABILITY STUDIES AT FOUR SUPERFUND SITES

by

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Contract No. 68-03-2766

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Selected wastewater treatment processes were evaluated in bench-scale tests using contaminated groundwaters and leachates from four hazardous waste problem sites. The processes investigated were selected on the basis of an extensive literature review and desktop analysis of 18 candidate processes. This preceeding work is described in a report entitled "Concentration Technologies for Hazardous Aqueous Waste Treatment" (EPA 600/2-81-019). The processes reported here include adsorption, biological treatment, coagulation and precipitation, filtration, ozonation, sedimentation, and stripping. The processes were used singly and in various process train configurations.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

Numerous unit processes have been tested and demonstrated for treating municipal wastewaters, and public and industrial water supplies. However, these applications do not accurately duplicate the conditions associated with contaminated groundwater and leachate treatment. The purpose of this research was to test the applicability of several unit processes to the types of groundwater and leachate currently being discovered and investigated around the country. The results of this investigation will aid future efforts to formulate viable, cost-effective solutions to groundwater contamination problems.

Selected wastewater treatment processes were evaluated in bench-scale tests using contaminated groundwaters and leachates from four hazardous waste problem sites. The processes investigated were selected on the basis of an extensive literature review and desktop analysis of 18 candidate processes. This preceding work is described in a report entitled "Concentration Technologies for Hazardous Aqueous Waste Treatment" (EPA 600/2-81-019). The processes reported here include adsorption, biological treatment, coagulation and precipitation, filtration, ozonation, sedimentation, and stripping. The processes were used singly and in various process train configurations.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

PREFACE

Our Nation faces a rising incidence of poor hazardous waste disposal practices that are harmful to groundwater resources and their beneficial uses. The contamination source must be controlled to mitigate further damage at a particular problem site. At many sites, it also is necessary to prevent further contaminant migration and to provide water of sufficient quality and quantity to meet user demands. One way to accomplish these goals may be treatment of the contaminated groundwater.

Numerous unit processes have been tested and demonstrated for treating municipal and industrial wastewaters, contamination resulting from sudden material spills, and public and industrial water supplies. However, these applications do not accurately duplicate the conditions associated with contaminated groundwater treatment. The purpose of this research was to test several unit processes judged in an earlier phase of this project to be most applicable to the types of groundwater problems currently being discovered and investigated around the country. Tests were conducted using contaminated waters from four problem sites for hazardous waste disposal. The intent was to investigate process performance under various wastewater matrix conditions -- not to optimize performance at a particular site. The work demonstrated that site-specific conditions must be investigated to evaluate process performance accurately.

The results of this investigation will aid future efforts to formulate viable, cost-effective solutions to groundwater contamination problems.

ABSTRACT

Selected wastewater treatment processes were evaluated in bench-scale tests using contaminated groundwaters and leachates from four hazardous waste problem sites. The processes investigated were selected on the basis of an extensive literature review and desktop analysis of 18 candidate processes. This preceding work is described in a report entitled "Concentration Technologies for Hazardous Aqueous Waste Treatment" (EPA 600/2-81-019). The processes reported here include adsorption, biological treatment, coagulation and precipitation, filtration, ozonation, sedimentation, and stripping. The processes were used singly and in various process train configurations.

Wastewaters used in the studies were obtained from the following problem hazardous waste disposal sites:

- Ott/Story Site, Muskegon, Michigan - Past chemical company disposal practices caused contamination of groundwater with dozens of organic priority pollutants, a large portion of which are volatile.
- Gratiot County Landfill, Gratiot County, Michigan - Polybrominated biphenyls were disposed of at a municipal/industrial landfill. Investigations had shown that PBB's had entered the groundwater.
- Marshall Landfill, Boulder, Colorado - Leachate from a municipal landfill containing industrial residues threatened a surface waterway that conveyed water from a reservoir to a public water supply system. Organic priority pollutants were found in the leachate.
- Olean Wellfield, Olean, New York - An aquifer serving as a municipal water supply source was contaminated with trichloroethylene.

Process performance was measured under a range of operating conditions. Total organic carbon (TOC) was generally used as a surrogate for routine process monitoring, but specific compounds were examined at selected times.

The report provides details of the study methods and process performance results. A general conclusion was that site-specific conditions greatly influence process performance. Thus site-specific studies should be conducted in most cases to evaluate and select a viable, cost-effective approach for a particular problem site.

This report was submitted in fulfillment of Contract No. 68-03-2766 by Michael Baker, Jr., Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period March, 1979 to December, 1983, and work was completed as of December, 1983.

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SECTION 1

INTRODUCTION

PROJECT BACKGROUND

This document is the third and final major report resulting from a program to evaluate and verify concentration techniques for hazardous constituents of aqueous waste streams. The first two were entitled: "Concentration Technologies for Hazardous Aqueous Waste Treatment," (EPA-600/52-81-019, March 1981), and "Management of Hazardous Waste Leachate" (EPA Technical Resource Document SW-871, September 1980). Taken together, the three reports mirror increased and significant attention focused on hazardous wastes during the past 4 to 5 years. Hence the following discussion is intended to describe not only how the three reports fit together, but also the historical setting that guided their formulation.

As originally conceived, this program was to identify, evaluate, and verify those promising technologies that could be used to concentrate relatively dilute hazardous aqueous waste streams before detoxification or disposal. Though this purpose has been maintained and successfully achieved within the context of the three reports, several major developments have had considerable impact on the focus of the overall program. For example, during the period when a contractor was being selected to conduct this program (summer of 1978), media attention first focused on Love Canal. Moreover, in the early stages of the project (spring of 1979), it became clear that Love Canal was not an isolated problem. Because of rising awareness of potential implications of poor hazardous waste disposal practices, reports of additional problem sites began to mount.

As a result of this growing concern, the House Subcommittee on Oversight and Investigation of the Interstate and Foreign Commerce Committee conducted hearings designed to determine the magnitude of the hazardous waste disposal site problem. Following the hearings, the subcommittee conducted a "Waste Disposal Site Survey" and issued their report in October 1979. The survey found that the 53 chemical companies queried (1,605 plants) produced approximately 66 million tons of process wastes in 1978 alone. Since 1950, these companies had disposed of about 762 million tons of chemical wastes in 3,383 locations. Of these sites, 32 percent (1,099) were known to be closed, and another 9 percent (319) may be closed. The closed-site inventory of wastes was believed to be about 100 million tons. Furthermore, it was estimated that about 4.8 million tons were taken by private haulers to unknown destinations.

In a separate assessment, the U.S. Environmental Protection Agency (EPA) concluded that between 30 and 40 million metric tons of hazardous wastes would be generated in 1980. This annual generation rate was expected to double by the year 2000. EPA believed that there were as many as 32,000 hazardous waste dump sites throughout the country. Of these, 1,200 to 2,000 were thought to present possible health or environmental problems.

These estimates prompted acute public concern, which resulted in (1) the promulgation of strict regulations in November 1979 implementing the provisions of the Resource Recovery and Conservation Act of 1976 (RCRA), and (2) passage of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). Eventually, in the fall of 1982, EPA issued a list of 419 abandoned hazardous waste sites, the cleanup of which would be funded by the $1.6-billion program known as the Superfund.

The present research program began just as the magnitude of the problems of hazardous waste sites were being recognized. The project progressed as knowledge of the nature of the problems started to become refined, and finally, program results were able to be focused at four Superfund sites. In these final stages, treatability studies were performed on actual groundwater and leachates contaminated by several different types of hazardous wastes. The end result of the program is that a number of unit processes capable of having broad application in concentrating aqueous contaminants at hazardous waste disposal sites were identified and evaluated. This report focuses on the final stages of the program in which these unit processes were demonstrated in bench-scale treatability studies for four Superfund sites. In one case, the treatability studies were conducted onsite for an 18-month period.

Before introducing the scope of work conducted in the final stages of the program, work conducted earlier in the project is briefly discussed.

EARLIER WORK

In work for the first report, "Concentration Technologies for Hazardous Aqueous Waste Treatment", it was found that the most widespread hazardous waste problem faced by the public sector is contamination from unsecured waste disposal sites. This contamination generally is in the form of leachates and contaminated ground and surface waters. However, there is no such thing as a "typical" hazardous waste problem--each site is unique. Research efforts showed that of the problem sites examined in the early stages of this project, wastes encountered were diverse in terms of composition and concentration--varying from site to site and often varying over time at any given site. Waste streams at some sites contained a broad spectrum of organic and inorganic compounds, while others had only a few constituents of concern. These waste streams generally fell into one of the following two composition categories: high organic - low inorganic or low organic - high inorganic.

On the basis of an extensive literature review and desktop analysis, the following unit processes were identified as having potential broad application in concentrating aqueous hazardous wastes:

- o biological treatment
- o carbon adsorption

- chemical coagulation
- membrane processes
- resin adsorption
- stripping.

Although not a concentration technology, because of its demonstrated ability to enhance treatability of numerous organic compounds, chemical oxidation (e.g., ozonation, possibly with UV irradiation) also was judged to have potential application. Generally, the above processes must be supplemented with ancillary processes such as sedimentation and filtration.

Because of the diversity of waste streams, it was evident that in most cases no single unit process would be sufficient to treat the contamination problems encountered. As a result, five process trains were formulated as being broadly applicable to most types of known contamination. These were:

- biological treatment/carbon sorption
- carbon sorption/biological treatment
- biophysical treatment
- membrane/biological treatment
- stripping/carbon sorption.

It further was concluded that because hazardous waste contamination problems differ substantially from place-to-place, treatability studies in some form almost always are a prerequisite to selection of an optimum treatment approach. Hence, in order to demonstrate the applicability of the unit processes and their combinations, it was decided that it was important to evaluate these methods at actual hazardous waste problem sites. Results of this decision are reported herein.

Based upon the findings of the first stages of this project described above, EPA requested that they be incorporated into a technical resource document on the "Management of Hazardous Waste Leachate". This manual was intended to provide guidelines for permit officials and owners and operators of hazardous waste management facilities. Leachate was defined as the liquid contained within a landfill or impoundment which percolates into surrounding soil and is collected for subsequent treatment.

The manual provided a logical thought process for arriving at reasonable treatment process trains for specific leachates. Furthermore, sufficient factual information was provided so that manual users could readily identify a few potential treatment alternatives which could be refined to make a final choice. The manual began with a brief discussion of factors that influence leachate generation. This was followed by data on leachate characteristics at actual waste disposal sites. Major options for dealing with hazardous waste leachate were identified.

A major section of the manual dealt with technology profiles for processes having potential application to leachate treatment. These process descriptions were supplemented by treatability data, information on by-products, costs, and process applicability. Factors which influence treatment process train selections and a suggested approach for systematically addressing such selections were discussed. A few hypothetical and actual leachate situations were used as examples for applying the approach to the selection of appropriate treatment processes. Other sections of the manual addressed monitoring, safety, contingency plans/emergency provisions, equipment redundancy/backup, permits, and surface runoff.

The manual was prepared concurrently with the treatability studies conducted at the Ott/Story site. As a result, the manual profited from experience gained during the laboratory and field work. Conversely, the manual helped to structure subsequent treatability studies at other locations.

TREATABILITY STUDIES

The capability of the unit processes identified as having potential, either individually or as process trains, to treat contaminated groundwater or leachates was demonstrated at four Superfund sites. These were:

- Ott/Story Site, Muskegon, MI
- Gratiot County Landfill, MI
- Marshall Landfill, Boulder County, CO
- Olean Wellfield, Olean, NY.

The objective was to investigate process performance under various wastewater matrix conditions -- not to optimize performance at a particular site. The work demonstrated that site-specific conditions must be investigated to evaluate process performance accurately. Results of these studies are the subject of this report.

At the Ott/Story site, groundwater was severely contaminated by numerous organic compounds. Because of the complex nature of the problem and the willingness of the current site owner to cooperate with EPA, extensive treatability studies were conducted on-site for an 18-month period. Activated carbon and resin adsorption, aerobic and anaerobic biological treatment, chemical oxidation, and stripping were investigated at the bench scale. The process train which performed best was granular activated carbon adsorption followed by activated sludge treatment. High levels of treatment were maintained for short periods of time.

The Gratiot County landfill problem involved contamination of groundwater by polybrominated biphenyls (PBB). PBB contamination was the result of the disposal of PBB in the landfill by a chemical company. Because PBB is relatively insoluble, PBB contamination was found to be associated primarily with sediment and not with the water in samples taken in this study. Therefore, it was concluded that physical separation processes should effect significant levels of PBB removal.

At the Marshall landfill site, low levels of hazardous material contamination were found within high-strength organic contamination indicative of sanitary landfills. The primary method used in these treatability studies was granular activated carbon sorption. Results of these efforts were inconclusive.

Groundwater at the Olean wellfield was contaminated by trichloroethylene from an unknown source. Treatability studies showed that air stripping was the most cost-effective method for removing the contaminant.

The report which follows describes the methodologies used at each of the four sites to screen treatment methods, discusses the advantages and disadvantages of the unit processes in differing situations, and recommends potential approaches for other applications.

SECTION 2

CONCLUSIONS

1. Each site with hazardous aqueous waste problems (e.g., leachates or contaminated surface or groundwater) is unique in terms of problem nature, magnitude, and potential solutions. Moreover, individual unit process performance is specific to the wastewater matrix, and this matrix cannot be accurately duplicated with a synthetic wastewater. Thus, treatability studies using actual site wastewaters were necessary for a good assessment of unit process performance and for development of process design criteria.

2. A single unit process is not capable of treating the complex wastewater matrix present at many problem sites. In such cases, a train of unit processes must be assembled.

3. The effluent quality objectives for treating hazardous waste leachates and contaminated groundwater must be assessed from several perspectives. In many cases, it was found that even though the effluent had a high TOC concentration (several hundred milligrams per liter), organic priority pollutants were absent at typical detection levels. The presence of non-priority organics and their impact when treated water is discharged either to a surface water body, groundwater, or publicly-owned treatment works (POTW'S) must be assessed. It may not be possible or necessary to attain the effluent TOC levels typically associated with POTW discharges. Attention should be focused instead on the toxicity and risk associated with a particular level of effluent quality, and this assessment should be integrated with the treatment process evaluation procedure to assure selection of a cost-effective treatment approach. Pursuing the assessment in this manner also necessitates that bench or pilot-scale treatability studies be conducted using site-specific wastewater.

4. Available literature describing the performance of unit processes is limited. Much of the currently published information describes evaluations using either single compound synthetic solutions or gross indicator parameters when a complex wastewater matrix is employed. Information from full-scale treatment operations is limited by the paucity of these operations and confidentiality constraints imposed by process vendors and private sector clients. Available literature can serve only as a starting point to design a site-specific evaluation study; it should not be used to decide the degree of treatment that can be achieved cost-effectively or for final design purposes. Information in this report should therefore be used for initial technology screening and for formulating site-specific evaluations, not for identifying the preferred option for a problem site, even if the situations are similar.

5. Air stripping successfully removed volatile organic priority pollutants. In one case, numerous volatile priority pollutants and in another case trichloroethylene were reduced from milligram/liter levels to non-detectable levels. Air emission considerations must be assessed on a case-by-case basis to determine process viability and cost-effectiveness.

6. For a groundwater having a high TOC concentration (480-610 mg/l), steam stripping resulted in a severalfold concentration of waste stream organics in the stripper overhead. However, bottoms stream flow was only six percent less than the feed flow and bottoms TOC ranged from 300 to 400 mg/l. This may have been due partly to operational limitations of the laboratory-scale apparatus.

7. Granular activated carbon (GAC) provided high degrees of organic priority pollutant removal. However, when treating a groundwater with a high TOC concentration (about 1,000 to 2,000 mg/l), GAC could not sustain high TOC removal levels. For example, TOC removal declined to less than 50 percent after processing five bed volumes; within 100 to 160 bed volumes, TOC removal decreased to 10 to 15 percent. Even when TOC removal had declined to 35 percent and effluent TOC was about 600 mg/l, generally greater than 98 percent organic priority pollutant removal still was attained.

8. Carbonaceous adsorption resins demonstrated TOC breakthrough characteristics similar to those of GAC. However, TOC breakthrough occurred more rapidly.

9. Biological treatment processes alone were capable of achieving only minimal TOC removal, even though attempts were made to acclimate the process and assure proper operating conditions. TOC removals by the activated sludge process slightly exceeded removals provided by air stripping alone. An anaerobic biological treatment process could not be sustained on raw contaminated groundwater even under conditions believed to be suitable for anaerobic processes. At the Ott-Story site, bioinhibitory substances rather than usable substrate limitations were believed to be responsible for affecting biological process performance.

10. GAC pretreatment of raw groundwater permitted development of an aerobic biological treatment process that was capable of further treating GAC effluent. Greater than 95 percent TOC removal was achieved by this process during the period in which GAC removal of TOC exceeded 30 percent. After this initial period, process train performance declined as GAC performance declined. Several organic priority pollutants were detected in off-gas from activated sludge reactors; these included methylene chloride, 1,2-dichloroethane, benzene, tetrachloroethylene, and toluene.

11. Anaerobic treatment (upflow anaerobic filter, UAF) of GAC-pretreated groundwater was possible, but performance declined as GAC performance declined. Overall, the GAC/UAF process train performed more poorly than the GAC/AS process train, with an upper TOC removal limit of 81 percent.

12. Pretreatment by ozone oxidation did not appear to enhance either adsorption or aerobic biological treatment processes.

13. Laboratory-scale tests generally require considerable quantities of wastewater. When actual wastewaters are being used, logistical problems may arise and errors may be introduced because of transformations during sample storage. Acceptable alternative preservation techniques are limited because most will affect unit process performance. Freezing samples shortly after collection and thawing them at room temperature just before use worked well for sample preservation in one situation and very poorly in another. Checks should be built into the technology evaluation studies to assess potential errors associated with the study methodology.

SECTION 3

GENERAL METHODOLOGY

TECHNOLOGY EVALUATION PROCEDURE

As described in Section 1, earlier phases of this work involved identification and desktop evaluation of unit processes potentially suitable for concentrating hazardous constituents of aqueous waste streams. Results of that evaluation have been published in a report entitled "Concentration Technologies for Hazardous Aqueous Waste Treatment" (1). The following conclusions from that report form the general premise for the technology evaluation activities reported herein:

- Concentration technologies judged to have the greatest broad spectrum potential are chemical precipitation, flocculation, sedimentation, filtration, biological treatment, carbon adsorption, and resin adsorption.
- Reverse osmosis, stripping, and ultrafiltration are believed to have more limited and specialized applicability.
- Ion exchange for removal of inorganic species also may have potential but usually, competing processes such as chemical precipitation are more economical.
- Since hazardous waste contamination problems differ substantially from place-to-place, treatability studies in some form are almost always a prerequisite to selection of an optimum treatment approach and/or for developing design criteria.
- Much of the experimental data on chemical treatability has been generated from pure compound systems. Removal from multicomponent systems may differ substantially.
- Several concentration processes are promising for treatment of hazardous aqueous wastes. However, for the application of interest, often a single unit process will not be sufficient. In such instances, process trains must be utilized.

Based upon these conclusions, it was decided that contaminant streams used for the technology evaluations should be representative of the matrices present at actual problem sites rather than pure compound systems. Synthesis of such complex matrices was judged to be infeasible because of the various nuances associated with actual contaminated groundwater and leachates. Consequently, it was decided that use of waters from actual hazardous waste problem sites would provide the most representative and useful information on the performance of treatment processes.

Technologies can be evaluated either at laboratory bench-scale or at pilot plant scale. Bench scale studies were used in this effort covering a wide range of independent variables because the objective was to assess the performance of a number of unit processes under various conditions and not to optimize a process for treating a particular waste stream.

Two alternative methods of conducting bench-scale technology evaluations were identified:

1. shipping contaminated water to the Baker/TSA laboratory for experimental studies, and

2. establishing a technology evaluation laboratory at the problem site.

During the course of this research, both approaches were used.

In most cases, laboratory evaluations began with batch tests of individual unit process. For selected unit processes or process combinations, batch sequential or continuous flow studies were undertaken. Physical-chemical systems were operated for sufficient periods of time to reflect steady state conditions. Biological treatment processes were operated to assure steady states with acclimated biocultures. Study procedures varied depending upon the contaminant stream being studied; details are discussed below.

Monitoring treatment process influent and effluent chemical characteristics was recognized at the outset to be potentially complex and costly. Much of the literature reviewed during the earlier phases of this contract described process performance on the basis of broad measurements such as COD and failed to address the effects on specific chemical compounds. Accordingly, it was recognized that specific compound data must be developed to improve the existing information base. To accomplish this within project time and budget constraints, indicator/surrogate parameter measurements were supplemented with specific compound analyses; the former were examined routinely and the latter were measured at critical times during process evaluations. Total Organic Carbon (TOC) was used as a surrogate when the wastewater was predominantly organic; either heavy metals or organic priority pollutants were analyzed when removal of specific compounds was of interest. TOC was selected as a surrogate parameter because accurate results could be obtained rapidly and relatively inexpensively; this allowed timely control of laboratory study direction. Analytical procedures are discussed in greater detail below.

SELECTION OF TESTING SITES

During the first phase of this contract, hazardous waste problem sites where public agencies are (or would be) involved in some capacity in remedial actions were identified (1). This effort enabled development of a list of potential sites for obtaining contaminated waters for technology evaluations. As the study progressed, additional problem sites were identified. If background data were provided and they indicated the presence of a problem potentially amenable to treatment by concentration technology, the site was added to the candidate list. Criteria used to select the test sites included:

- availability of quantitative data describing problem nature and magnitude,
- absence of pending litigation which would limit information transfer,
- cooperative relationships between current site owners and the regulatory agencies, and
- intention to undertake, or at least study, implementation of remedial measures.

Using these criteria, the following sites were selected as sources of contaminated water for bench-scale technology evaluations:

- Ott/Story Site, North Muskegon, Michigan;
- Gratiot County Landfill, Bethany Township, Michigan;
- Marshall Landfill, Boulder County, Colorado; and
- Olean Wellfield, Olean, New York.

Descriptions of each of these sites and the investigations undertaken using each wastewater are presented in more detail elsewhere in this report. Table 1 summarizes site characteristics and the technologies examined.

ANALYTICAL PROCEDURES

As stated earlier, TOC was used regularly as a surrogate parameter to monitor organics in a gross fashion while specific organic and inorganic compound analyses were performed at selected times. In addition, several parameters were measured frequently to characterize operating conditions of the unit process being tested.

TOC was measured with an Ionics Model 1258 Total Carbon - Total Organic Carbon Analyzer. All samples were analyzed almost immediately after collection. Except for vacuum filtration of selected unit process effluents to remove suspended solids and required dilution to allow analysis on the preferred instrument detection scale, there was no preservation, modification, or storage of samples prior to testing. Before selection of vacuum filtration for solids separation, potential stripping of volatile organics was examined.

TABLE 1. SITE CHARACTERISTICS AND STUDY SUMMARY

Item	Ott/Story North Muskegon, Michigan	Gratiot County Landfill Bethany Township, Michigan	Marshall Landfill Boulder, Colorado	Olean Wellfield Olean, New York
SITE CHARACTERISTICS:				
Waste Stream	contaminated groundwater	contaminated groundwater	seepage draining from landfill	contaminated groundwater
Pollutants of Concern	numerous organic priority and non-priority constituents	PBB and several heavy metals	numerous organic priority pollutants	trichloroethylene (TCE)
Laboratory Study Location	on-site	Baker/TSA lab, Beaver, PA	Baker/TSA lab, Beaver, PA	Baker/TSA lab, Beaver, PA
Waste Stream Sampling	samples withdrawn from two existing wells; collected as needed at 1 to 3 day intervals	withdrawn from existing well by state agency staff	sampled by county agency staff at pond constructed to impound seepage	sampled by project staff and municipal employees at discharge line from city water well
Sample Handling	samples from individual wells composited for lab studies	shipped to Baker/TSA on several occasions in 5 gal expanded polypropylene carboys immediately after collection; generally received one day after collection	shipped to Baker/TSA on several occasions in 5 gal expanded polypropylene carboys immediately after collection; generally received one day after collection	shipped to Baker/TSA initially in 0.5 gal glass bottles; later 275 gal shipped in 55 gal drums
Sample Storage	generally stored 1 to 3 days in glass or polyethylene containers	carboys frozen upon receipt; thawed at room temperature when needed	initially carboys were frozen upon receipt; however, because of significant TOC loss during thawing, unopened carboys from subsequent samplings were stored at room temperature until used	stored in closed sampling container at room temperature until used

(Continued)

TABLE 1. (Continued)

Item	Ott/Story North Muskegon, Michigan	Gratiot County Landfill Bethany Township, Michigan	Marshall Landfill Boulder, Colorado	Olean Wellfield Olean, New York
TECHNOLOGIES EXAMINED:				
adsorption				
granular activated carbon	X	X	X	X
powdered activated carbon	X			X
resins	X		X	X
biological				
activated sludge	X		X	
trickling filter	X			
anaerobic filter	X			
coagulation/precipitation	X			
filtration	X	X		
ozonation	X			
stripping				
air	X		X	X
steam	X			
sedimentation	X	X		
unit processes combined into process trains	X	X	X	

Organic priority pollutant analyses were performed by more than one laboratory during the course of this contract. All analyses were performed according to EPA protocol (2,3) using combined gas chromatography-mass spectrometry (GC-MS) and gas chromotography (GC).

Heavy metal analyses were performed by Baker/TSA using flame or graphite furnace atomic absorption spectrophotometry techniques. Other analyses during the project (e.g., pH, suspended solids, ammonia nitrogen) were in accordance with Standard Methods (4).

EXPERIMENTAL APPARATUS

The technologies itemized in Table 1 were evaluated at the bench scale using equipment matching the conditions to be investigated. The following briefly describes the experimental procedures and apparatus used in the evaluation of each technology; additional details are provided when the site-specific results are presented.

It should be noted that throughout this report, units of measure which typically are associated with unit process operation have been used; for example, hydraulic loading to granular activated carbon columns is reported in gallons per minute per square foot of surface area. A table to convert to the International System of Units (SI) is provided in Table 2.

Adsorption - Activated Carbon

Granular Activated Carbon --

Granular activated carbon (GAC) adsorption studies generally began with batch isotherm testing followed by continuous flow, small diameter column studies. Isotherm tests were undertaken to determine:

- comparative performance of different sorbents,
- approximate contact times,
- effect of wastewater composition matrix, and
- approximate sorbent dose rates.

Data were used to develop Freundlich adsorption isotherms according to the equation:

$$x/m = kc^{1/n}$$

Where: x = amount of solute adsorbed

m = weight of carbon

c = equilibrium concentration of solute in solution after adsorption

k, n = constants

TABLE 2. CONVERSION FACTORS

To Convert From Customary Unit	Multiply By	To Obtain SI Unit
cf	2.832×10^{-2}	m^3
ft	3.048×10^{-1}	m
°F	(°F-32) 0.5556	°C
gal	3.785×10^{-3}	m^3
gal	3.785	1
gpd	3.785×10^{-3}	m^3/Day
gpd	3.785	1/day
gpm	6.308×10^{-5}	m^3/s
gpm	6.308×10^{-2}	1/s
gpm/sf	6.790×10^{-4}	$m^3/s/m^2$
gpm/sf	6.790×10^{-1}	$1/s/m^2$
inch	2.54×10	mm
lb	4.536×10^{-1}	kg
lb/1000 cf	1.602×10	g/m^3
lb/day/cf	1.602×10	$kg/day/m^3$
lb/day/sf	4.883	$kg/day/m^2$
sf	9.290×10^{-2}	m^2

Continuous flow studies were undertaken to examine the effects of hydraulic and solute loading rates, and contact times, and to develop solute breakthrough curves.

Two granular activated carbon sorbents were used during the course of this study:

- Filtrasorb 300 (FS-300) - Calgon Corporation
- GAC 30 - Carborundum Corporation

Properties of these carbons are summarized in Table 3.

For isotherm tests, carbons were used in the powdered form. Granular carbons were pulverized and screened; that portion passing through 325 mesh screen was used for isotherm tests. After classification, the powdered carbon was oven dried overnight at 105°C, cooled, and stored in a desiccator until needed. A slurry of this powdered carbon was prepared with distilled water and used in the isotherm tests.

For batch isotherm tests, an aliquot of contaminated water and the desired dose of carbon were contacted in capped glass bottles of 100 or 250 ml capacity. Mixing was accomplished using a platform shaker operated at either 180 or 280 excursions/minute depending upon the carrier tray load. Mixing time and wastewater pH also were varied during the studies. After the prescribed contact period, powdered carbon was removed by filtration through Whatman #2 paper, Wastewater pH was adjusted only at the start of the contact period.

It should be noted that preliminary tests investigated mixing with a six-paddle stirrer at 100 rpm and with a magnetic stirrer. However, these techniques were not utilized because they did not provide adequate contact at high sorbent doses and allowed release of volatile organics from the open 900 ml glass beakers.

For the continuous flow studies, 1.90 or 2.54 cm diameter glass columns operated individually and in series were used. Bed height was varied by arranging the columns in series. Sampling ports were provided before the first column, at mid-points between columns in series, and after the last column. Feedwater was pumped to the first column either from a storage container or an upstream process using a chemical metering pump; column effluent was discharged to laboratory drains, fed directly to a subsequent treatment process, or stored and fed over a period of time to a post-treatment process. Prior to filling the columns, a weighed amount of GAC was mixed with distilled water and soaked to degas the carbon. Columns then were charged and backwashed. Studies were conducted under a vented hood when volatile constituents were known or suspected to be present in the wastewater. Figure 1 illustrates a typical GAC continuous flow experimental apparatus.

TABLE 3. GRANULAR ACTIVATED CARBON PROPERTIES

PROPERTIES	GAC Filtrasorb 300	 GAC 30
U.S. Standard Series Sieve Size		
Larger than No. 8 (max.)	15%	15%
Smaller then No. 30 (max.)	4%	5%
Iodine Number (mg/g) (min.)	900	900
Abrasion Number (min.)	75	70
Mean Particle Diameter (min.)	1.5 - 1.7	1.5 - 1.7
Effective Size (mm)	0.8 - 0.9	0.85
Water Soluble Ash (max.)	0.5%	NA
Moisture Content (max.)	2.0%	2.0%
Base Material	bituminous coal	coal
Total Surface Area (N_2 BET Methanol, m^2/gm)	950 - 1050	900 - 1000
Apparent Density (lb/ft^3)	NA	32
Backwashed and Drained Density (lb/ft^3)	26 - 27	27

NOTE: Properties defined by manufacturer's specification literature.

NA: Not Available

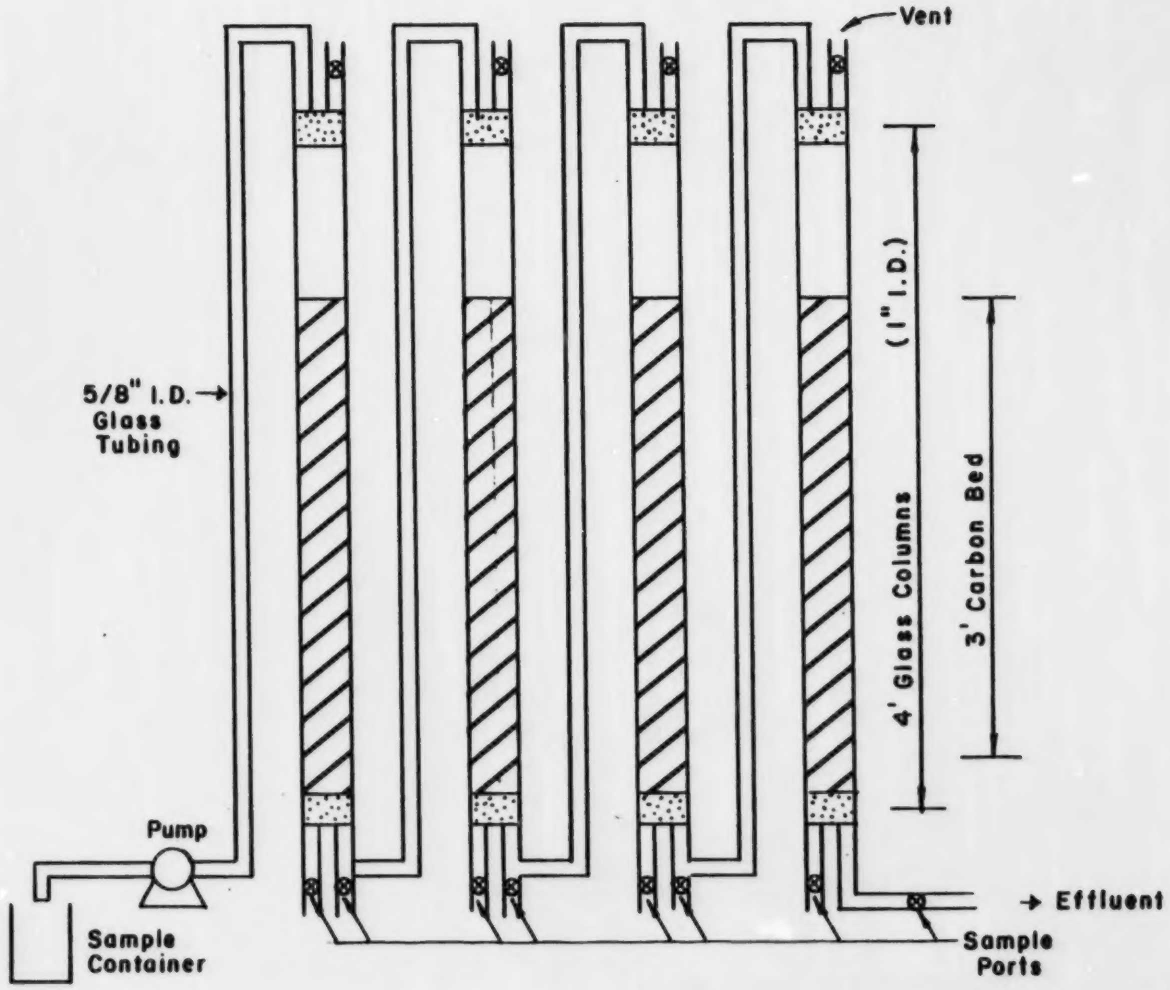

Vent
5/8" I.D. Glass Tubing
(1" I.D.)
4' Glass Columns
3' Carbon Bed
Pump
Sample Container
Effluent
Sample Ports

Figure 1. Typical GAC Continuous Flow Experimental Apparatus.

Powdered Activated Carbon --

Studies of powdered activated carbon (PAC) also involved batch isotherm tests as described for GAC studies. However, continuous flow studies involved addition of PAC to activated sludge reactors for concurrent adsorption and biological treatment.

The two carbons used for these studies were:

- Hydrodarco C (HDC) - ICI Americas, Inc.
- Nuchar SA - Westvaco

Table 4 summarizes properties of these carbons.

In continuous flow studies, PAC was added to the aeration chamber of the activated sludge reactor and removed from the settling chamber with the settled sludge floc. Various PAC doses were tested; study conditions also were controlled to evaluate various hydraulic retention times and activated sludge mixed liquor suspended solids concentrations. Operation of the activated sludge system is described later.

Adsorption - Resin

Batch isotherm and continuous flow column adsorption studies were conducted using the following polymeric and carbonaceous resins produced by Rohm and Haas Corporation:

- Amberlite XAD 4 - polymeric
- Ambersorb XE 340 - carbonaceous
- Ambersorb XE 347 - carbonaceous
- Ambersorb XE 348 - carbonaceous

Properties of these resins are presented in Table 5.

Isotherm and column studies were conducted in a manner similar to those described previously for GAC.

Biological Treatment

Biological treatment processes investigated included:

- activated sludge
- trickling filter
- upflow anaerobic filter

TABLE 4. POWDERED ACTIVATED CARBON PROPERTIES

TYPICAL PROPERTIES	PAC Hydrodarco C	 Nuchar S-A
Partical Size (min % -325 mesh)	70	65-85
Tamped Density (g/ml)	0.70	NA
Apparent Density (kg/m^3)	NA	385-415
Surface Area (m^2/gm)	550	1400-1800
pH	10.5	4-6
Water Solubles (%)	5.5	3-4
Ash (%)	NA	4-8
Total Pore Volume (cm^3/g)	NA	2.2-2.5
Base Material	lignite	
Iodine Number (min)	NA	800

NOTE: Properties defined by manufacturer's specification literature.

NA: Not Available

TABLE 5. PROPERTIES OF ADSORPTION RESINS

PROPERTIES	Ambersorb XE-340	Ambersorb XE-347	Ambersorb XE-348	Amberlite XAD-4
Appearance	black, spherical non-dusting	black, spherical non-dusting	black, spherical non-dusting	hard, hydrated opaque beads
Total Surface Area (N_2 BET method M^2/gm)	400	350	500	725
Bulk Density (lbs/cu ft)	37	43	37	44
Particle Density (g/cm³) (Hg displacement)	0.92	1.05	0.91	
Skeletal Density (g/cm³) (Hg displacement	1.34	1.85	1.95	1.08
Pore Volume (g/cm³)	0.34	0.41	0.58	
Particle Size (U.S. Sieve Series	20-50	20-50	20-50	20-60
Crush Strength (kg/Particle)	GT 3.0	GT 3.0	1.0	
Ash Content (%)	LT 0.5	LT 0.5	LT 0.5	
Average Particle Diameter (mm)				0.30-0.45
True Wet Density in Distilled Water (gm/l)				1.02
Average Pore Diameter (Angstroms)				40

NOTE: Properties defined by manufacturer's specifications.
GT: Greater Than
LT: Less Than

Activated sludge process investigations included conventional activated sludge, conventional activated sludge with the addition of powdered activated carbon (PAC) to the aeration chamber, and activated sludge seeded with Phenobac®, a commercial mutant bacteria product. All biological systems were operated on a continuous flow basis using either raw wastewater or wastewater pretreated in different ways. Attempts were made to acclimate the systems to the wastewater being investigated prior to assessing process performance.

For activated sludge studies, either 350 ml Swisher reactors (Figure 2) or one liter reactors (Figure 3) were used. The smaller reactors generally were used to screen the feasibility of aerobic biological treatment or when available wastewater quantities were limited, necessitating reduced throughputs while still operating at the desired hydraulic and organic loading rates and retention times. They also facilitated examination of the extent of stripping of volatile organics due to aeration because two Swisher units, one operated with activated sludge biomass and one containing only wastewater, could easily be operated in parallel. It should be noted that several problems were experienced with the Swisher reactors:

- Because flow rates were small, the quantity of effluent produced over a reasonable period of time greatly limited effluent analytical testing options.
- Close control of the mixed liquor suspended solids (MLSS) was difficult because the quantity of sample required for MLSS analysis would severly deplete the volume of sludge remaining in the reactor.

Despite these problems, the reactors were relatively easy to maintain and useful for screening the feasibility of aerobic biological treatment.

Larger reactors were used during the PAC addition studies, when longer duration runs were intended, when larger quantities of treated effluent were required for priority pollutant analyses, and when better mixed liquor suspended solids (MLSS) control was desired.

Two sizes of trickling filter apparatus were used: a 4.9 cm diameter by 58 cm long plexiglass column, and a 2.54 cm by 122 cm glass column. Each contained a rock media and was operated in a downflow mode. Although this configuration facilitated influent dosing, maintaining an aerobic environment proved to be difficult. The filter discharged to a clarifying apparatus from which settled sludge was recycled back to the filter or wasted. Because of difficulties associated with their operation and poor performance, studies using a trickling filter were terminated and are not discussed further herein.

Anaerobic biological treatment was investigated using a heated, packed bed anaerobic filter operated in an upflow mode. Figure 4 schematically illustrates the reactor and gas collection system. Operating criteria are discussed in Section 4 where process performance is reviewed.

For the aerobic systems, seed sludge initially was obtained from municipal wastewater treatment facilities. To acclimate the biomass, the processes

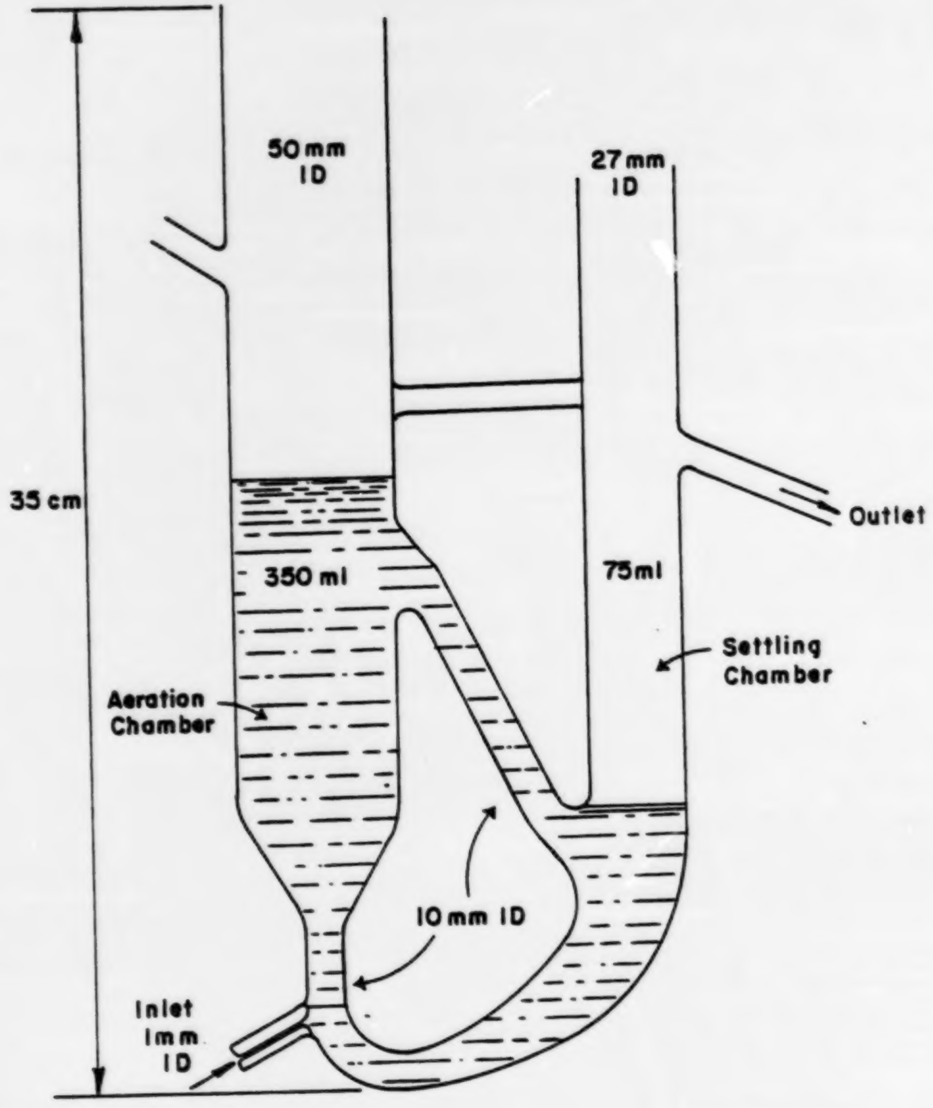

50mm
ID
27mm
ID
35 cm
Outlet
350 ml
75ml
Settling
Chamber
Aeration
Chamber
10mm ID
Inlet
1mm
ID

Figure 2. Davis-Swisher Reactor

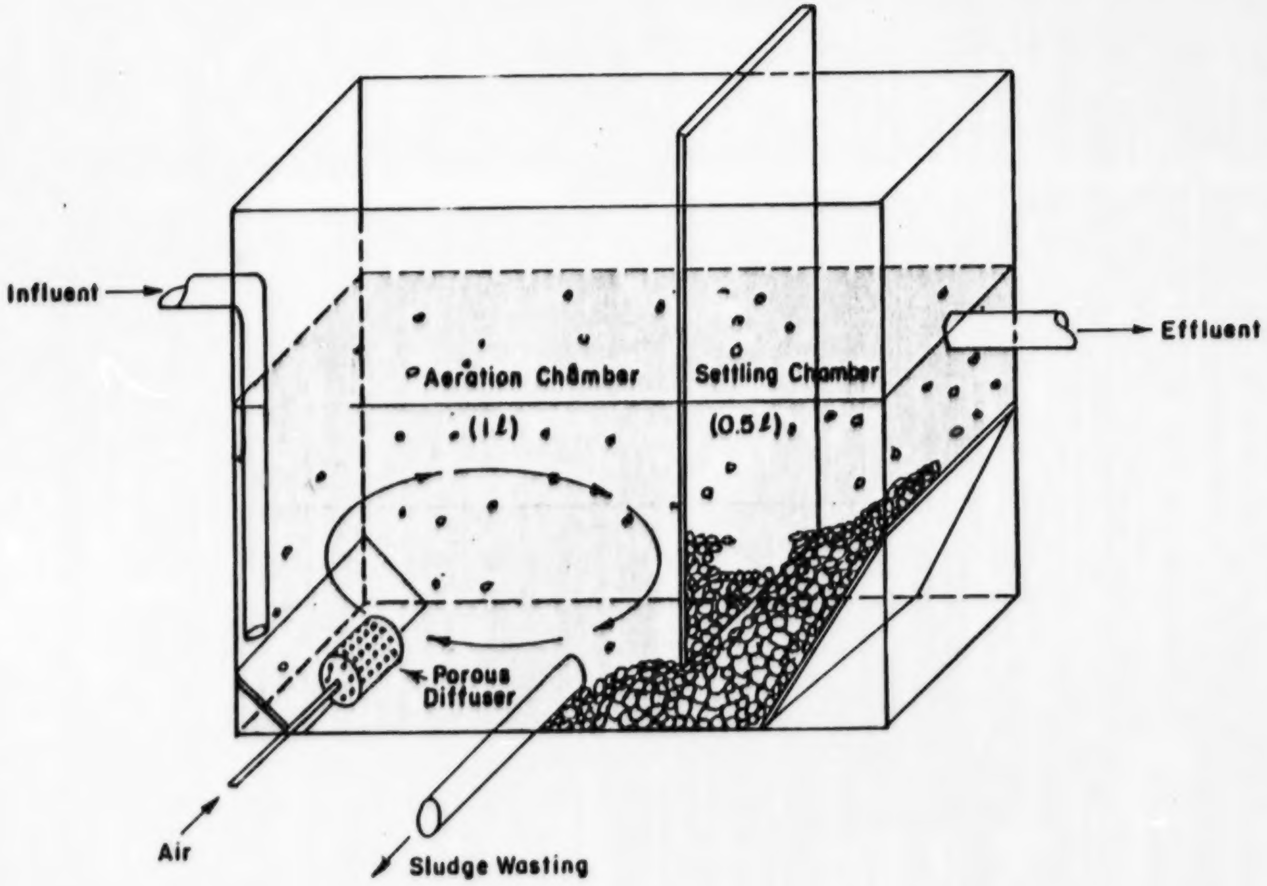

Influent
Aeration Chamber
(1ℓ)
Settling Chamber
(0.5ℓ)
Effluent
Porous Diffuser
Air
Sludge Wasting

Figure 3. One Liter Biological Reactor.

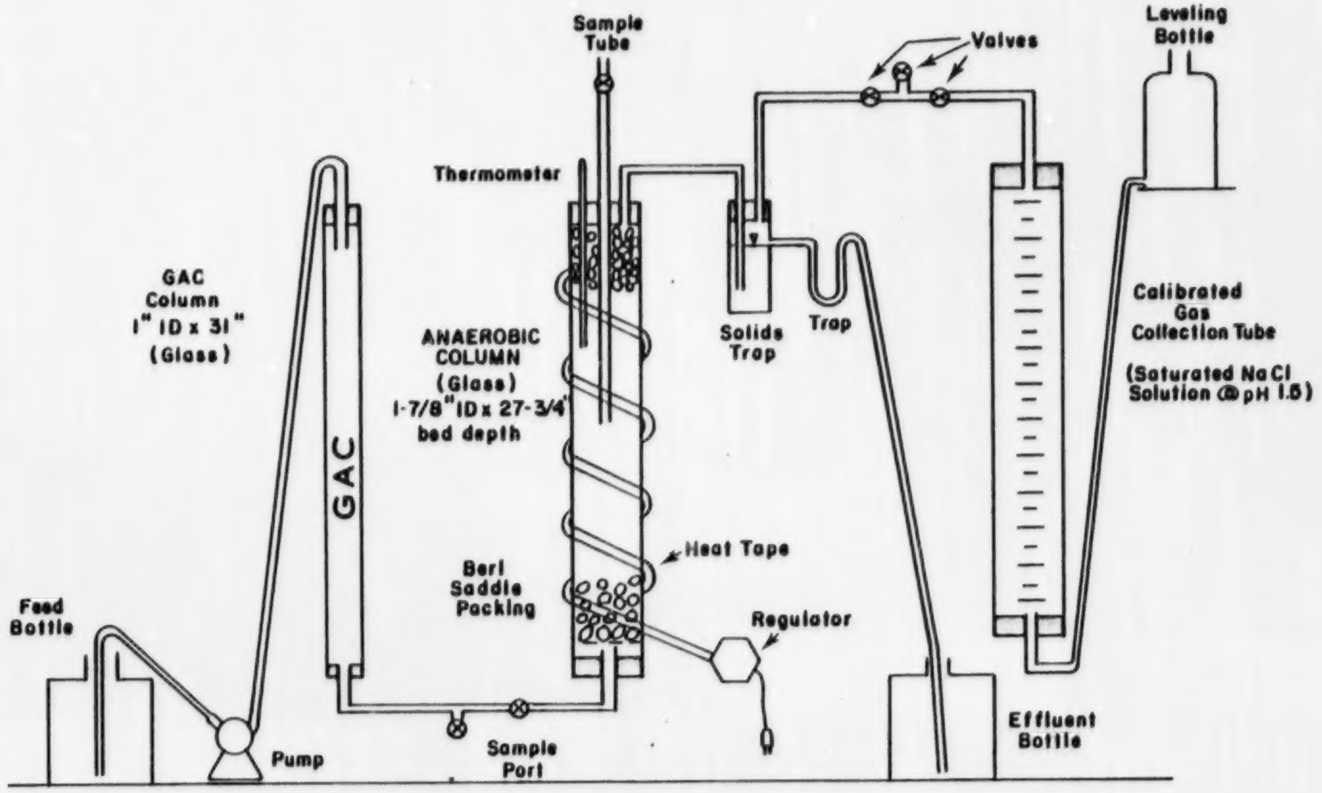

Sample Tube
Valves
Leveling Bottle
Thermometer
GAC Column 1" ID x 31" (Glass)
ANAEROBIC COLUMN (Glass) 1-7/8" ID x 27-3/4" bed depth
Solids Trap
Trap
Calibrated Gas Collection Tube
(Saturated NaCl Solution @ pH 1.5)
GAC
Heat Tape
Beri Saddle Packing
Feed Bottle
Regulator
Pump
Sample Port
Effluent Bottle

Figure 4. GAC/Anaerobic Filter Schematic.

were operated on a municipal wastewater feed for some period of time and then were gradually converted to the feedwater being used in the investigation. When necessary, feedwater composition was modified by pH adjustment (with dilute phosphoric or sulfuric acid) and nutrient addition.

The anaerobic filter initially was filled one-half full with sludge from a well-operated municipal wastewater treatment sludge anaerobic digester and operated for eight days on raw municipal sewage before converting to groundwater pretreated by GAC adsorption. Feed later was converted to raw contaminated groundwater. Operating details are given in Section 4.

Filtration

When wastewaters contained suspended solids that were expected to interfere with the operation of the primary treatment process (e.g., plugging of GAC adsorption column), granular media filtration was used for pretreatment. Columns of various sizes were loaded with white sand which passed a No. 40 sieve (<0.0165 in. particle size) and operated in a gravity downflow mode.

Ozonation

Evaluation of ozonation was conducted on a batch basis. The process was used as the primary treatment process and as a pretreatment technology. Figure 5 illustrates a schematic of the ozonation assembly. A Welsbach Model T-408 laboratory scale ozone generator was operated under the following conditions:

- ozone production using air feed
- ozone gas flow rate - 2 l/min
- ozone dose - approximately 2 g/hr (generator operating at 90 volts)
- glass reactor vessel with fritted glass diffusers
- batch volume - 7.5 to 15 l.

Studies using contaminated groundwater began after preliminary studies with distilled water to assure good mixing and ozone transfer. Ozone measurements were made according to Standard Methods (4) using the Iodometric Method.

Stripping

Air Stripping --

Air stripping techniques included diffused aeration as well as stripping under mechanical mixing and quiescent conditions in open containers. Air stripping generally was investigated whenever stripping was judged to be one of several avenues of contaminant removal associated with a particular treatment technology; for example, during diffused aeration activated sludge treatment or ozonation. In these situations, either a stripping reactor was

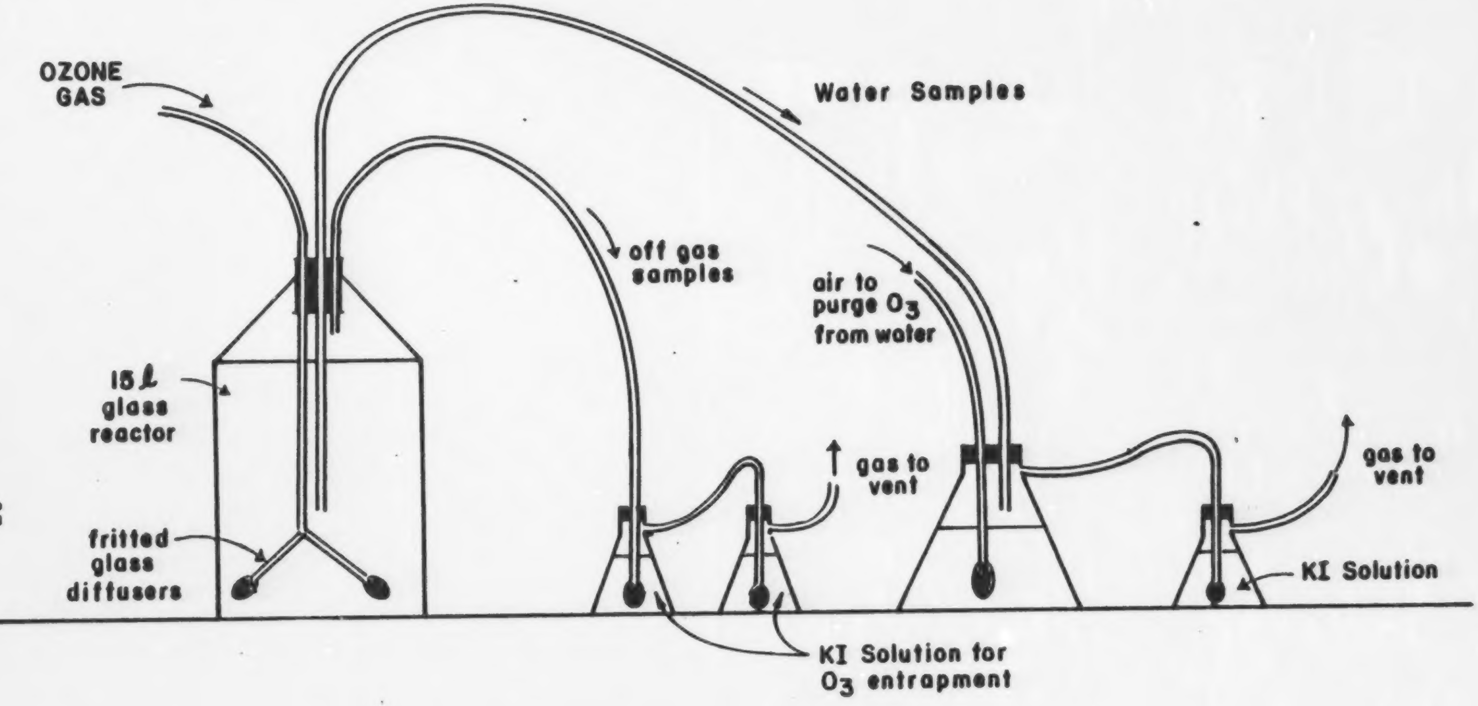
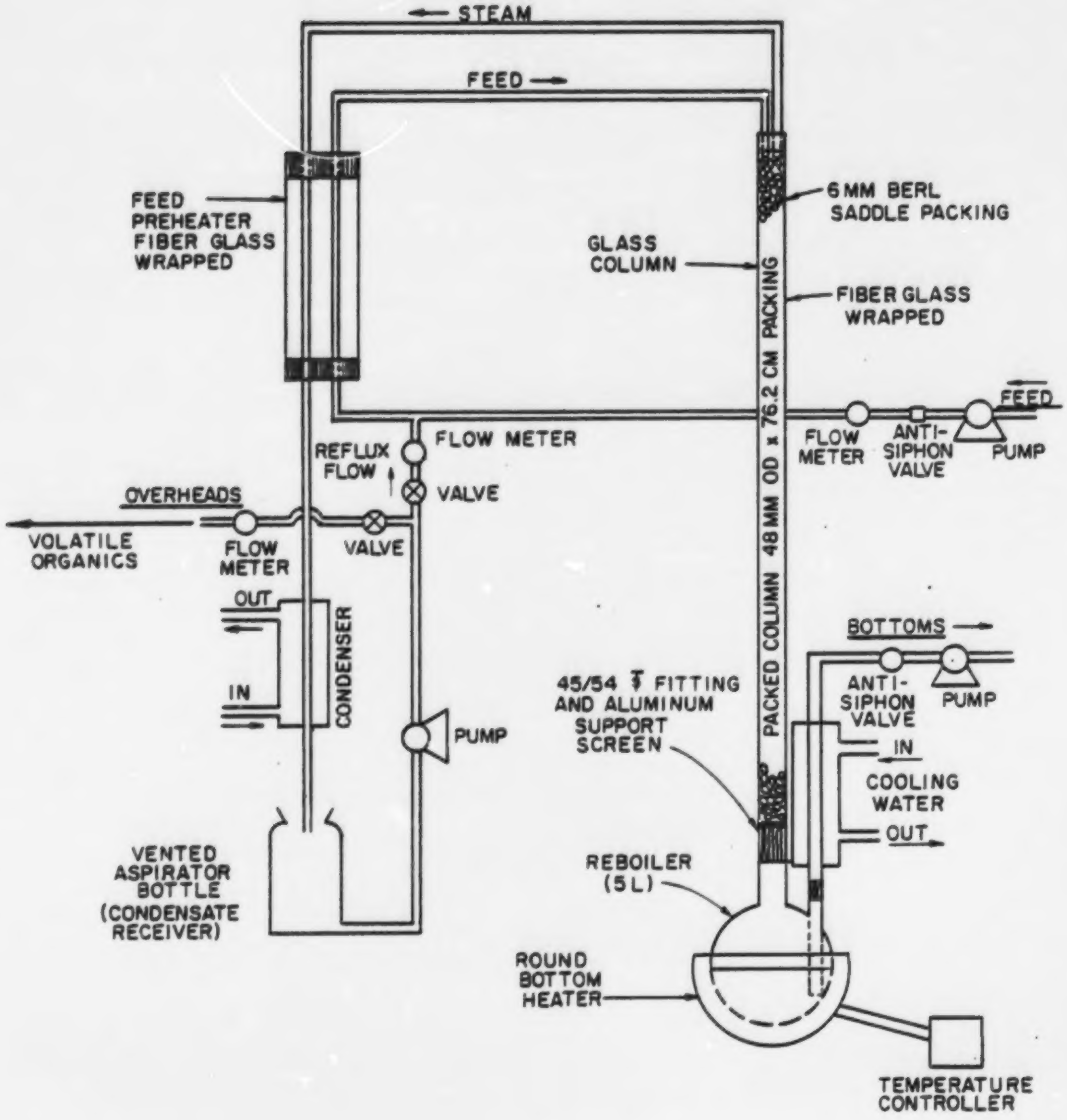

OZONE GAS
Water Samples
off gas samples
air to purge O_3 from water
15 ℓ glass reactor
gas to vent
gas to vent
fritted glass diffusers
KI Solution
KI Solution for O_3 entrapment

Figure 5. Schematic of Ozonation Assembly.

operated in parallel with the primary process being investigated (for activated sludge a parallel Swisher or larger reactor was operated) or the primary process reactor was operated solely to investigate stripping (the ozonation reactor was operated with air rather than ozone).

Steam Stripping --

A packed column, continuous flow apparatus was used to evaluate steam stripping; Figure 6 illustrates a schematic of the system. Although numerous variables affect system performance, the primary operation parameters investigated were feed flow rate and overhead flow rate. Maintenance of steady state conditions proved to be difficult and the apparatus was not capable of operating in the desired overhead to feed flow ratio range of 0.02 to 0.05. Operating and performance details are discussed in Section 4.



STEAM
FEED
FEED PREHEATER FIBER GLASS WRAPPED
6 MM BERL SADDLE PACKING
GLASS COLUMN
FIBER GLASS WRAPPED
PACKED COLUMN 48 MM OD x 76.2 CM PACKING
FEED
FLOW METER
ANTI-SIPHON VALVE
PUMP
FLOW METER
REFLUX FLOW
VALVE
OVERHEADS
VOLATILE ORGANICS
FLOW METER
VALVE
OUT
IN
CONDENSER
PUMP
BOTTOMS
ANTI-SIPHON VALVE
PUMP
45/54 ₮ FITTING AND ALUMINUM SUPPORT SCREEN
IN
COOLING WATER
OUT
VENTED ASPIRATOR BOTTLE (CONDENSATE RECEIVER)
REBOILER (5 L)
ROUND BOTTOM HEATER
TEMPERATURE CONTROLLER

Figure 6. Continuous Flow, Packed Column Steam Stripping Apparatus.

SECTION 4

STUDIES USING CONTAMINATED GROUNDWATER FROM THE OTT/STORY SITE

BACKGROUND

At the Ott/Story site in North Muskegon, Michigan, groundwater has been contaminated by the disposal and poorly controlled storage of chemical production wastes by previous owners of a chemical production facility. The present owner, Cordova Chemical Company, cooperated with the State of Michigan in carrying out efforts to remove contamination sources; characterize site geohydrology, groundwater quality, and contaminant plume migration; and identify and evaluate remedial action options for management of contaminated groundwater. Results of the study described herein were made available to the Michigan Department of Natural Resources (DNR) as they evolved to assist that agency in its evaluations. Subsequently, the Ott/Story site was declared a Superfund site by the U.S. Environmental Protection Agency.

Most of the technology evaluations discussed herein were performed using composite samples obtained from two wells in the contamination plume: wells OW9 and W17d. Groundwater composition differed substantially at the two well locations as illustrated by the data contained in Table 6. Groundwater composition at other points in the plume also varied widely from that reported in Table 6. Table 7 presents a summary of contaminated groundwater composition data measured at various points in the plume.

Identified organic compounds at the measured concentrations listed in Table 6 do not account for the measured TOC concentrations.

Chromatographs of several GC/MS analyses for priority pollutants in samples from studies using composite groundwater from wells OW9 and W17d were examined to investigate the presence of non-priority organics. Several phenolic, aniline, phthalate, and organic acid compounds were indicated. However, because extraction procedures used for priority pollutant analyses are not suitable for extracting all non-priority organic compounds, other organics present cannot be identified and thus, a comprehensive estimate of constituents comprising groundwater TOC cannot be prepared. The legal and health effects significance of non-priority pollutants in raw groundwater, and in partially treated groundwater are unknown.

TECHNOLOGY EVALUATIONS

As described in Section 3 and summarized in Table 1, the following technologies were evaluated using groundwater from the Ott/Story site:

TABLE 6. COMPARISON OF ORGANIC POLLUTANT ANALYSIS OF RAW GROUNDWATER FROM WELLS OW9 AND W17d (mg/l)*

Parameter	Well OW9	Well W17d
Vinyl Chloride (P)	2.33	0.044
Methylene Chloride (P)	0.60	0.086
1,1-Dichloroethylene (P)	0.18	0.044
1,1-Dichloroethane (P)	1.03	0.12
Chloroform (P)	0.87	0.20
1,2-Dichloroethane (P)	103.	5.58
1,1,1-Trichloroethane (P)	0.13	0.05
2-Ethoxypropane	0.18	ND
Trichloroethylene (P)	0.01	ND
Benzene (P)	0.12	1.83
Perchloroethylene (P)	0.01	0.15
Toluene (P)	0.24	0.29
Chlorobenzene (P)	0.022	ND
2-Chlorophenol (P)	0.12	0.051
Phenol (P)	0.091	0.087
Benzyl Alcohol	0.06	ND
Benzoic Acid	6.80	ND
Hexanic Acid	0.95	ND
Cresol	ND	0.065
Methyl Propyl Phenols	37.	18.
1,2-Dichlorobenzene (P)	ND	1.6
Aniline	0.089	0.075
Methyl Aniline	2.6	ND
n,n-Dimethyl Aniline	19.6	29.
2-Chloroaniline	0.075	ND
Camphor	20.7	16.
Benzonitrile	0.019	ND
Substituted Benzenes	9.7	11.
1,4-Dichlorobenzene (P)	ND	0.075
TOC	1620-2400	171-270

(P) - a priority pollutant
ND - not detected at a detection limit of 0.010 mg/l
* - Wells located about 900 feet apart within the contamination area; typical analysis

TABLE 7. OTT/STORY SITE GROUNDWATER GENERAL CHARACTERIZATION

Parameter	Composition Range**
pH	10-12
BOD	300 - 1600 mg/l
COD	5400 - 8300 mg/l
TOC	200 - 2100 mg/l
NH_3-N	50 - 200 mg/l
Organic N	110 mg/l
Chloride	500 - 4100 mg/l
Conductivity	18,060 µmhos/cm
TDS	12,000 mg/l
Volatile Organics:	
Vinyl chloride*	140 - 32,500
Methylene chloride*	<5 - 6570
1,1-Dichloroethylene*	60 - 19,850
1,1-Dichloroethane*	<5 - 14,280
1,2-Dichloroethane*	0.350 - 111 mg/l
Benzene*	6 - 7800
1,1,2-Trichloroethane*	<5 - 790
1,1,2,2-Tetrachloroethane*	<5 - 1590
Toluene*	<5 - 5850
Ethyl benzene*	<5 - 470
Chlorobenzene*	<5 - 140
Trichlorofluoromethane*	<5 - 18
Chloroform	1400
Trichloroethylene	40
Tetrachloroethylene	110
Acid Extractable Organics:	
o-Chlorophenol*	<3 - 20
Phenol*	<3 - 33
o-sec-Butylphenol***	<3 - 83
p-Isobutylanisol*** or p-Acetonylanisol***	<3 - 86
p-sec-Butylphenol***	<3 - 48
p-2-oxo-n-Butylphenol	<3 - 1357
m-Acetonylanisol***	<3 - 1546
Isopropylphenol***	<3 - 8
1-Ethylpropylphenol	<3
Dimethylphenol*	<3
Benzoic acid	<3 - 12,311

(Continued)

TABLE 7. (continued)

Parameter	Composition Range**
Methylphenol	40
Methylethylphenol	20
Methylpropylphenol	210
3,4-D-Methylphenol	160
Base Extractable Organics:	
Dichlorobenzene*	<10 - 172
Dimethylaniline	<10 - 17,000
m-Ethylaniline	<10 - 7640
1,2,4-Trichlorobenzene*	<10 - 28
Naphthalene*	<10 - 66
Methylnaphthalene	<10 - 290
Camphor	<10 - 7571
Chloroaniline	<10 - 86
Benzylamine or o-Toluidine	<10 - 471
Phenanthrene* or Anthracene*	<10 - 670
Methylaniline	310

*A priority pollutant
**All concentrations in μg/l except as noted
***Structures not validated by actual compound

- adsorption - granular activated carbon
  - powdered activated carbon resins

- biological treatment - activated sludge
  anaerobic filter

- ozonation

- stripping - air
  - steam

Efforts commenced with preliminary investigations focused on pretreatment by neutralization, chemical coagulation, and precipitation; methods of solids/liquid separation; and volatility concerns. Following this, batch studies of individual unit processes were undertaken. Sequential batch studies and continuous flow studies of one unit process and trains of processes then were undertaken.

In the following sub-sections, results are organized and reported primarily by unit process. However, because numerous process train evaluations were made, it is most useful to report certain results by process train rather than by individual unit process.

Preliminary Studies

Results of preliminary batch investigations in the area of chemical neutralization, coagulation, and precipitation first are summarized below.

1. Small amounts of fine sediment and silt were present in the groundwater samples. This material did not have associated measurable TC or TOC content. It settled slowly under quiescent as well as stirred conditions. Attempts to coagulate this sediment with ferric chloride and several polymers produced no effect either in appearance or in TOC reduction in the supernatant liquid.

2. Samples in contact with 5 gm/l powdered activated carbon for five minutes filtered more readily and appeared clear and colorless, even when TOC removals were less than 15 percent.

3. Samples stored for two days in full, sealed glass flasks showed TOC reductions of 0 to 7 percent.

4. Reductions in TC and TOC concentrations in raw groundwater by separation using vacuum filtration, gravity filtration, and centrifuging all were very slight. Vacuum filtration was selected for use in subsequent studies (when solid/liquid separation of this type was necessary) because it was the most convenient technique and did not appear to induce significant stripping of volatile organics.

5. Studies on volatilization of organics were conducted for periods of 48 hours using open quiescent, stirred, air sparged, and closed

containers at the prevailing groundwater pH of about 10 and adjusted pH values of 7.5 and 6.0 with the following results:

a. less than 7 percent TOC reductions in closed containers,

b. 20 to 25 percent TOC loss from quiescent samples at all pH values and from stirred and sparged samples at pH 10.

c. 40 percent TOC loss from stirred and sparged samples at pH values of 6.0 and 7.5.

The preliminary investigations led to the conclusion that careful sample handling was necessary to minimize experimental error due to loss of volatile organics and for protection of laboratory personnel. All work was conducted in fume hoods using glass containers to the maximum extent possible.

Air and Steam Stripping

Since chlorinated hydrocarbons were of key concern at the Ott/Story site, technologies found useful in the treatment of similar constituents in drinking waters seemed appropriate for use in this research. Techniques for the removal of halogenated hydrocarbons from drinking water previously have been summarized (5). Ott/Story site groundwater differed qualitatively from drinking water in that it contained chlorinated hydrocarbons, aromatics and simple organic acids analogous to drinking water "chlorinated hydrocarbon precursors", and uncharacterized high molecular weight "non-priority" pollutants.

Simple aeration and steam stripping are considered viable approaches for volatile halogenated hydrocarbon removal in drinking water (5). Since most of the priority pollutants at the Ott/Story site were associated with the volatile fraction (Tables 6 and 7), air stripping would provide the simplest approach for removal of bulk hazardous constituents. Steam stripping with reflux would provide a greater degree of volatile halogenated hydrocarbon removal and also allow for recovery and concentration of such materials in the condensed overhead stream thus abating a potential air pollution problem.

Air Stripping--

Air stripping experiments were carried out in a series of 2.5 l Plexiglas reactors which were equipped with porous airstones to sparge the groundwater. Data shown on Table 8 illustrate that all volatile priority pollutants were reduced to non-detectable levels after air sparging. In addition, activated carbon treatment of the air sparged effluent resulted in virtually complete removal of the remaining base neutral and acid fraction priority pollutants. Therefore, it was concluded that technology similar to that suggested by EPA for drinking water applications (5), would be applicable to removal of priority pollutants from the Ott/Storage groundwater. However, a significant organic residual as measured by TOC remained after air stripping and the air stripping/carbon sorption batch treatment sequences.

TABLE 8. REMOVAL OF GROUNDWATER ORGANIC POLLUTANTS BY AIR STRIPPING

		Concentration in:		
Type	Compound	Raw Groundwater	Air Sparging Effl[1]	Sparge and Carbon Sorption Effl[2]
V	Methylene Chloride	0.07	ND	0.50*
V	1,1-Dichloroethane	1.6	ND	ND
V	1,1-Dichloroethylene	1.0	ND	ND
V	Chloroform	2.0	ND	ND
V	1,2-Dichloroethane	14	ND	0.01
V	1,1,1-Trichloroethane	0.28	ND	ND
V	Trichloroethylene	0.05	ND	ND
V	Benzene	5.3	ND	ND
V	Perchloroethylene	0.19	ND	ND
V	Toluene	3.6	ND	ND
V	Chlorobenzene	0.18	ND	ND
V	Ethylbenzene	0.02	ND	ND
V	1,1,2-Trichloroethane	0.05	ND	ND
B/N	Dichlorobenzene	0.05	ND	ND
B/N	Methylaniline	0.24	0.53	ND

(Continued)

TABLE 8. (continued)

		Concentration in:		
Type	Compound	Raw Ground-water	Air Spar-ging Effl[1]	Sparge and Carbon Sorp-tion Effl[2]
B/N	Ethylanilene	3.8	0.60	ND
B/N	Trichloro-benzene	0.01	ND	ND
B/N	Naphthalene	0.01	ND	ND
B/N	Dimethyl-aniline	15.0	0.61	0.08
B/N	Camphor	3.9	0.47	0.01
A	Chlorophenol	0.03	0.01	ND
A	Phenol	0.01	0.01	ND
A	Methylphenol	0.04	0.03	ND
A	Methylethyl-phenol	0.02	0.02	ND
A	Methylpro-pylphenol	0.28	0.28	ND
A	3,4-Dimethyl-phenol	0.12	0.14	ND
A	Benzoic Acid	0.30	0.02	ND
	TOC	720	641	

Footnotes:

[1] Air sparge for 48 hr at pH 6.0

[2] Air sparge for 48 hours at pH 6.0 followed by 2 hr contact with 50 g/1 dose of FS 300 carbon

V = Volatile Priority Pollutant
B/N = Base neutral extracted fraction
A = Acid extracted fraction
ND = Not detected (detection limit - 0.01 mg/l)
* = Possible sample contamination during extraction

Steam Stripping--

Figure 6 illustrates the continuous flow, packed column steam stripping apparatus. Independent operating variables were reboiler temperature and overhead:feed flow ratio. The apparatus was operated at feed stream flow rates of 40 to 80 ml/min, overhead (condensate) flow rates of 3.5 to 9.2 ml/min (overhead:feed flow ratios of 0.064 to 0.14), influent TOC concentrations of 480 to 610 mg/l, and time durations of 1 to 4 hours after establishing steady-state operation within the available operational controls.

Figure 7 presents a summary of results on a TOC basis. Average TOC in the stripper bottoms ranged from 300 to 400 mg/l and was virtually independent of overhead to feed ratio. This represented an approximate 34 percent overall TOC concentration from feed stream to stripper bottoms.

Steam stripping resulted in a concentrated overhead product which, at an overhead:feed ratio of 5 percent, had a TOC of about 4,000 mg/l. This represents a concentration of organics by a factor of 10 to 13 times and flow reduction to 5 percent of the feed value. While the laboratory-scale distillation column experienced stability problems at overhead:feed ratio of less than 6.4 percent, commercial scale units can operate at much lower ratios, thus providing for even further enrichment of the volatile priority pollutant and TOC fractions.

Conclusions regarding steam stripping are summarized below:

- Stream stripping is an energy intensive operation with marginal environmental advantages over simple aeration.
- Steam stripping removed a greater fraction of TOC from the bulk flow than air stripping. Air sparging resulted in about 11 percent volatilization of TOC from the bulk flow with removal of virtually all volatile priority pollutants. Steam stripping resulted in removal of about 34 percent of TOC from the bulk flow with recovery of these organics in a more concentrated overhead product.
- The environmental health and regulatory significance of materials remaining in air and steam stripper bottoms are unknown. The environmental health and regulatory significance of air emissions of small quantities of volatile priority pollutants also are unclear. Air stripping appears to be an acceptable pretreatment technique if air emissions are judged insignificant. Aerated groundwater may require further treatment for oxygen demand, trace organic, and heavy metal removal before discharge.
- As will be shown below, while air stripping was considered an excellent choice for the fourth site studied (Olean, N.Y.), it did not appear to completely resolve problems at the Ott/Story site.

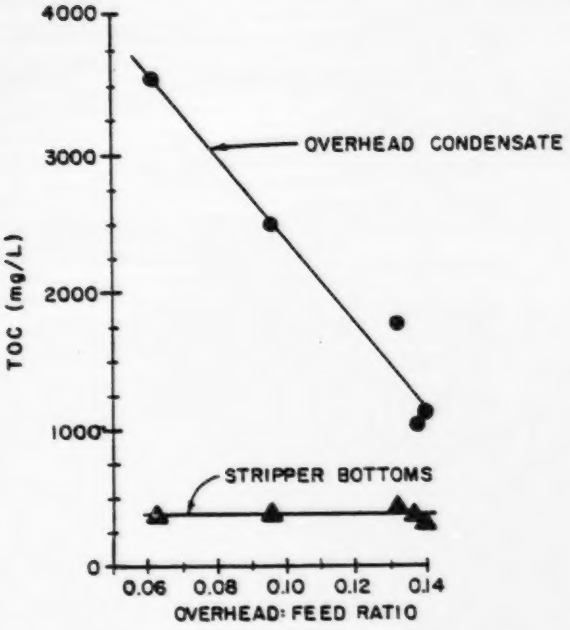


Figure 7. Continuous Steam Stripping of Contaminated Groundwater at Study Site.

Adsorption

Isotherm Studies--

Table 9 summarizes isotherm studies completed and study conditions for each. Tests were performed using raw groundwater (including composites and individual samples from wells OW9 and W17d) and groundwater pretreated by aeration, ozonation, biological treatment, and various sorbents. Variables investigated included sorbent, sorbent dose, pH, and contact time. Results are presented in Tables 10 through 17; isotherm data are plotted according to the Freundlich equation on Figures 8 through 15.

Prior to conducting the studies listed in Table 9, preliminary tests were performed which indicated that:

- Adsorption equilibrium is achieved after about 2 hours and 4 hours of contact for carbons and resins, respectively.
- Sorbents did not contribute significant concentrations of soluble organics to adsorption study filtrates. In studies in which distilled water was contacted with powdered FS-300 carbon and XE-347 resin, filtrate TOCs were 0 and 21 mg/l, respectively.

Examination of the isotherm batch contact study data resulting from use of raw composite groundwater indicates the following:

- Freundlich isotherms for all sorbents are steeply sloping straight lines when plotted on a logarithmic scale.
- Generally, carbons had slightly greater adsorption capacities than the resins at all pH values studied. In addition, carbons were capable of achieving slightly lower effluent TOC concentrations than were the resins.
- With regard to TOC removal efficiencies, carbons all performed about the same (See Table 10). Greater removals were observed at pH 10 and pH 4 than at pH 7.
- XE-347 performed slightly better than the other resins, with slightly better TOC removal at pH 4. In part, the poor wetting of XE-340 may have affected its performance.
- No sorbent was capable of achieving greater than 62 percent TOC removal even at sorbent doses as high as 100 g/l.

These results show that sorption alone is not capable of achieving high degrees of TOC removal from raw groundwater. This, in part, could be expected based on the presence of numerous soluble, low molecular weight organic compounds in the groundwater.

Similar, although less extensive, isotherm studies were completed using composite groundwater pretreated by aeration, ozonation plus activated sludge,

TABLE 9. SUMMARY OF ISOTHERM STUDIES

Wastewater	Carbon Sorbents - Study Conditions							Resin Sorbents - Study Conditions						
	Sorbent	pH	doses (g/l)	Contact Time (hr)	Initial TOC (mg/l)	Results on Table	Results on Figure	Sorbent	pH	doses (g/l)	Contact Time (hr)	Initial TOC (mg/l)	Results on Table	Results on Figure
Raw Composite (OW9/W17d)	FS 300	9.85	0.5, 5, 50, 100	2	603	10	8	XAD-4	10	0.5, 5, 50, 100	4	715	11	8
		7.	0.5, 5, 50, 100	2	641	10	9		7	0.5, 5, 50, 100	4	567	11	9
		4.	0.5, 5, 50, 100	2	690	10	10		4	0.5, 5, 50, 100	4	551	11	10
	HDC	9.85	0.5, 5, 50, 100	2	603	10	8	XAD-347	10	0.5, 5, 50, 100	4	715	11	8
		7.	0.5, 5, 50, 100	2	641	10	9		7	0.5, 5, 50, 100	4	567	11	9
		4.	0.5, 5, 50, 100	2	690	10	10		4	0.5, 5, 50, 100	4	551	11	10
	GAC 30	9.85	0.5, 5, 50, 100	2	603	10	8	XE-340	10	0.5, 5, 50, 100	4	715	11	8
		7.	0.5, 5, 50, 100	2	641	10	9		7	0.5, 5, 50, 100	4	567	11	9
		4.	0.5, 5, 50, 100	2	690	10	10		4	0.5, 5, 50, 100	4	551	11	10
	Nuchar S-A	10.1	1, 5, 15, 30, 50	2	736	10	8	XE-347(a)	9.7	25	4	638	15	8
	HDC	6.5	50	3.5	600	14	9							
	FS-300	6.5	50	3.5	600	14	9							
Composite (OW9/W17d) pretreated by aeration	FS 300	9.6	0.5, 5, 50, 106	2	940	12	11	XAD-4	9.6	0.5, 5, 50, 106	2	940	12	11
	HDC	6.	5	2.5	346	14	11							
	FS-300(a)	6.	50	2	641	15	11							
Composite (OW9/W17d) pretreated by ozonation	FS 300	9.6	0.5, 5, 50, 106	2	985	12	11	XAD-4	9.6	0.5, 5, 50, 106	2	985	12	11
								XE-340	9.6	0.5, 5, 50, 106	2	985	12	11
								XE-347	9.6	0.5, 5, 50, 106	2	985	12	11
Composite (OW9/W17d) pretreated by ozonation and activated sludge	FS 300	(b)	0.5, 5, 50, 100	2	282	13	12							
Composite (OW9/W17d) pretreated by upflow anaerobic filter	FS 300	(c)	0.5, 5, 50, 100	2	592	13	12							

(Continued)

TABLE 9. (Continued)

Wastewater	Carbon Sorbents - Study Conditions							Resin Sorbents - Study Conditions						
	Sorbent	pH	doses (g/1)	Contact Time (hr)	Initial (mg/1)	Results on Table	Results on Figure	Sorbent	pH	doses (g/1)	Contact Time (hr)	Initial (mg/1)	Results on Table	Results on Figure
Composite (OW9/W17d) pretreated by HDC carbon adsorption								XE-347	8	50	1	288	4-9	4-5
Composite (OW9/W17d) pretreated by XE-347 resin adsorption	FS 300(a)	9.7	50	2	455	15	11							
OW9 Groundwater	FS 300	9.4	5, 10, 50, 100	4	1820	16	13	XAD-4	9.4	100	4	1820	16	13
		7.0	5, 10, 50, 100	4	1820	16	13		7.0	100	4	1820	16	13
	HDC	9.4	5, 10, 50, 100	4	1820	16	13	XE-340	9.4	100	4	1820	16	13
		7.	5, 10, 50, 100	4	1820	16	13		7	100	4	1820	16	13
	Nuchar S-A	9.4	5, 10, 50, 100	4	1820	16	13	XE-347	9.4	100	4	1820	16	13
		7.0	5, 10, 50, 100	4	1820	16	13		7.0	100	4	1820	16	13
	FS 300	9.6	5	0.5, 1, 2, 4	2047		-							
OW9 Groundwater pretreated by activated sludge	FS 300	8.1	5	1	1077	15								
W17d Groundwater	FS 300	9.5	5	0.5,1, 2, 4	250			XAD-4	9.5	5	0.5, 1, 2, 4	250		
		9.4	0.5, 5, 50	1	230	16	15		9.4	5	1	230	16	15
		7.	0.5, 5, 50	1	220	16	14		7	5	1	220	16	14
	HDC	9.5	5	0.5,1, 2, 4	250			XE-340	9.5	5	0.5, 1, 2, 4	250		
		9.4	0.5, 5, 50	1	230	16	15		9.4	5	1	230	16	15
		7.	0.5, 5, 50	1	220	16	14		7	5	1	220	16	14
	Nuchar S-A	9.5	5	0.5,1, 2, 4	250			XE-347	9.5	5	0.5, 1, 2, 4	250		
		9.4	0.5, 5, 50	1	230	16	15		9.4	5	1	230	16	15
		7.	0.5, 5, 50	1	220	16	14		7	5	1	220	16	14

(Continued)

TABLE 9. (Continued)

Wastewater	Carbon Sorbents - Study Conditions							Resin Sorbents - Study Conditions						
	Sorbent	pH	doses (g/l)	Contact Time (hr)	Initial (mg/l)	Results on Table	Results on Figure	Sorbent	pH	doses (g/l)	Contact Time (hr)	Initial (mg/l)	Results on Table	Results on Figure
W17d Groundwater pretreated by activated sludge	FS 300	7.7	5	1	99	15								

(a) Organic priority pollutants also analyzed

(b) pH not recorded, estimated to be 7.3 to 7.6

(c) pH not recorded, estimated to be 7.2 to 7.4

TABLE 10. CARBON SORPTION ISOTHERM DATA USING RAW COMPOSITE GROUNDWATER

SORBENT	DOSE M(g/l)	TOC C_f (mg/l)			TOC SORBED x (mg/l)			LOADING X/M (mg/g)			TOC REMOVAL (%)		
		pH 9.85	pH 7.0	pH 4.0	pH 9.85	pH 7.0	pH 4.0	pH 9.85	pH 7.0	pH 4.0	pH 10.0	pH 7.0	pH 4.0
BLANK	0	603	641	690							16.4	13.1	14.1
FS 300	0.5	504	557	593	99	84	97	198	168	194	35.7	31.7	39.0
	5.0	388	441	421	215	200	269	43.0	40.0	53.8	55.9	49.1	52.8
	50.0	266	326	326	337	315	364	6.74	6.30	7.28	58.9		
	100.0	248	-	-	355	-	-	3.55	-	-			
HDC	0.5	574	635	641	29	6	49	58.0	12.0	98.0	4.8	0.9	7.1
	5.0	457	502	526	146	139	164	29.2	27.8	32.8	24.2	21.7	23.8
	50.0	306	362	367	297	279	323	5.94	5.58	6.46	49.3	43.5	46.8
	100.0	271	-	-	332	-	-	3.32	-	-	55.1		
GAC 30	0.5	541	575	599	62	66	91	124	132	182	10.3	10.3	13.2
	5.0	370	454	417	233	187	273	46.6	37.4	54.6	38.6	29.2	39.6
	50.0	271	326	308	332	315	382	6.64	6.30	7.64	55.1	49.1	55.4
	100.0	230	-	-	373	-	-	3.73	-	-	61.9		
Nuchar S-A		pH 10.1											
	0.0	736											
	1.0	653			83			83.0			11.3		
	5.0	558			178			35.6			24.2		
	15.0	491			245			16.3			33.3		
	30.0	452			284			9.47			38.6		
	50.0	429			307			6.14			41.7		

TABLE 11. RESIN SORPTION ISOTHERM DATA USING RAW COMPOSITE GROUNDWATER

SORBENT	DOSE M(g/l)	TOC C_f (mg/l)			TOC SORBED x (mg/g)			LOADING X/M (mg/l)			TOC REMOVAL (%)		
		pH 10.0	pH 7.0	pH 4.0	pH 10.0	pH 7.0	pH 4.0	pH 10.0	pH 7.0	pH 4.0	pH 10.0	pH 7.0	pH 4.0
BLANK	0	715	567	551									
XAD-4	0.5	654	517	511	61	50	40	122	100	80	8.5	8.8	7.3
	5.0	593	455	433	122	112	118	24.4	22.4	23.6	17.1	19.8	21.4
	50.0	487	388	365	228	179	185	4.56	3.6	3.7	31.9	31.6	33.6
	100.0	448	-	-	267	-	-	2.67	-	-	37.3		
XE-347	0.5	598	528	517	117	39	34	234	78	68	16.4	6.9	6.2
	5.0	570	438	399	145	129	152	29.0	25.8	30.4	20.3	22.8	27.6
	50.0	404	292	264	311	275	287	6.22	5.5	5.7	43.5	48.5	52.1
	100.0	331	-	-	384	-	-	3.84	-	-	53.7		
XE-340	0.5	670	534	534	45	33	17	90.0	66	34	6.3	5.8	3.1
	5.0	620	494	483	95	73	68	19.0	14.6	13.6	13.3	12.9	12.3
	50.0	537	449	376	178	118	175	3.56	2.4	3.5	24.9	20.8	31.8
	100.0	537	-	-	178	-	-	1.78	-	-	24.9		

TABLE 12. ISOTHERM DATA FOR COMPOSITE GROUNDWATER PRETREATED BY OZONATION OR AERATION

SAMPLE	SORBENT	SORBENT DOSE M(g/l)	FINAL TOC C_f(mg/l)	TOC SORBED X(mg/l)	SORBENT LOADING X/M(mg/g)	OVERALL TOC REMOVAL(%)*
Raw Groundwater			1050			
Groundwater after ozonation			1020			
Groundwater after aeration			1020			
Pretreated by Ozonation	FS 300	0	985			
		0.5	900	85	170	14.3
		5	815	170	34	22.4
		50	633	352	7.0	39.7
		106	573	412	3.9	45.4
	XAD 4	0.5	984	1	2	6.3
		5	942	43	8.6	10.3
		50	882	103	2.1	16.0
		106	852	133	1.2	18.9
	XE-340	0.5	970	15	30	7.6
		5	950	35	7	9.5
		50	920	65	1.3	12.4
		106	888	97	0.9	15.4
	XE-347	0.5	985	0	0	6.2
		5	930	55	11	11.4
		50	830	155	3.1	21.0
		106	730	255	2.4	30.5
Pretreated by Aeration (2.5 hr aeration)	FS 300	0	940			
		0.5	876	64	128	16.6
		5	754	186	37.2	28.2
		50	609	331	6.6	42.0
		106	560	380	3.6	46.7
	XAD 4	0.5	925	15	30	11.9
		5	912	28	5.6	13.1
		50	850	90	1.8	19.0
		106	767	173	1.6	27.0

* Calculated on the basis of raw groundwater TOC and final TOC after adsorption.

TABLE 13. ISOTHERM DATA FOR COMPOSITE GROUNDWATER PRETREATED ANAEROBIC FILTER BY OZONATION/ACTIVATED SLUDGE AND UPFLOW

SORBENT DOSE M(g/l)	FINAL TOC C_f (mg/l)	SORBENT LOADING X/M (mg/g)	TOC REMOVAL BY SORPTION (%)
Sample: Effluent from Ozonation/Activated Sludge, TOC of 282 mg/l (Raw Groundwater TOC was 606 mg/l)			
0	274	-	-
0.5	233	82	15
5	144	26	47
50	20	5.1	93
100	6	2.7	98
Sample: Effluent from Upflow Anaerobic Filter, TOC of 592 mg/l (Raw Groundwater TOC was 778 mg/l)			
0	592	-	-
0.5	530	124	10
5	475	23.4	20
50	337	5.1	43
100	289	3.0	51

Raw Groundwater:	50/50 Composite of OW9 and W17d
Sorbent:	FS 300
Contact Time:	2 hr

TABLE 14. TOC REMOVAL DURING SEQUENTIAL BATCH STUDIES OF SORPTION AND AIR STRIPPING

	STUDIES		
	Aeration followed by Carbon Sorption	Carbon Sorption followed by Aeration	Carbon Sorption followed by Resin Sorption
Conditions of Study	Aerate 48 hr at initially adjusted pH 6.0; 5 g/l dose HDC carbon for 2.5 hr at pH 6.0	50 g/l dose FS 300 carbon for 3.5 hr at initially adjusted pH 6.5; aerate 48 hr at pH 8.0 to 8.75	50 g/l dose HDC carbon for 3.5 hr at initially adjusted pH 6.5; 50 g/l dose XE-347 resin for 1 hr at pH 8.0
Results	Initial TOC: 650 TOC after aeration: 346, TOC after sorption: 199 (C_f)	Initial TOC: 600 TOC after sorption: 259 (C_f), TOC after aeration: 189	Initial TOC: 600 TOC after carbon sorption: 288 (C_f) TOC after resin sorption: 237 (C_f)
	First step TOC removal: 47%	First step TOC removal: 57%	First step TOC removal: 52%
	Overall TOC removal: 69%	Overall TOC removal: 68%	Overall TOC removal: 60%
Sorbent Loading (mg/g)	29.4	6.82	First step: 6.24 Second step: 1.02

TABLE 15. REMOVAL OF TOC AND AND SPECIFIC ORGANIC POLLUTANTS[5] DURING SEQUENTIAL BATCH STUDIES

	Pollutant Concentration (mg/l)					
	Study A[1]			Study B[2]		
Compound	Raw Wastewater	Resin Sorption Effluent	Carbon Sorption Effluent	Raw Wastewater	Aeration Effluent	Aeration Carbon Sorption Effluent
TOC	638	455	332	720	641	301
Methylene Chloride	0.06	ND	ND	0.07	ND	0.50[3]
1,1-Dichloroethane	1.2	ND	ND	1.6	ND	ND
1,1-Dichloroethylene	0.06	ND	ND	1.0	ND	ND
Chloroform	1.4	ND	ND	2.0	ND	ND
1,2-Dichloroethane	111	0.23	0.01	14[4]	ND	0.01
1,1,1-Trichloroethane	0.12	ND	ND	0.28	ND	ND
Tricholoroethylene	0.04	ND	ND	0.05	ND	ND
Benzene	7.8	0.17	0.01	5.3	ND	ND
Perchloroethylene	0.11	ND	ND	0.19	ND	ND
Toluene	2.6	ND	ND	3.6	ND	ND
Chlorobenzene	0.14	ND	ND	0.18	ND	ND
Ethylbenzene	0.01	ND	ND	0.02	ND	ND
1,1,2-Trichloroethane	0.16	ND	ND	0.05	ND	ND

(Continued)

TABLE 15. (continued)

	Pollutant Concentration (mg/l)					
	Study A[1]			Study B[2]		
Compound	Raw Wastewater	Resin Sorption Effluent	Carbon Sorption Effluent	Raw Wastewater	Aeration Effluent	Aeration Carbon Sorption Effluent
Dichlorobenzene	0.09	ND	ND	0.05	ND	ND
Methylaniline	0.31	ND	ND	0.24	0.53[4]	ND
Ethylaniline	3.3	ND	ND	3.8	0.60	ND
Trichlorobenzene	0.01	ND	ND	0.01	ND	ND
Naphthalene	0.01	ND	ND	0.01	ND	ND
Dimethylaniline	17.0	0.25	ND	15.0	0.61	0.08
Camphor	4.0	0.04	ND	3.9	0.47	0.01
Chlorophenol	0.02	ND	ND	0.03	0.01	ND
Phenol	0.01	ND	ND	0.01	0.01	ND
Methylphenol	0.04	ND	ND	0.04	0.03	ND
Methylethylphenol	0.02	ND	ND	0.02	0.02	ND
Methylpropylphenol	0.21	ND	ND	0.28	0.28	ND
3,4-Dimethylphenol	0.16	ND	ND	0.12	0.14	ND
Benzoic Acid	0.17	ND	0.18[4]	0.30	0.02	ND
Sorption Capacity (mg/g)		7.32	6.12			6.8
TOC Removal (%)		29	27[6]			53[6]

NOTES

1 Study A involved resin sorption followed by carbon sorption. Conditions during the study stages were:

Sorbent:	XE-347	FS 300
Dose:	25 g/1	50 g/1
Contact Time:	4 hr	2 hr
Wastewater pH:	9.7	9.7

2 Study B involved treatment by aeration followed by carbon sorption. Aeration accomplished by sparging for 48 hr at pH 6; aeration effluent contacted with FS 300 carbon at 50 g/1 dose for 2 hr.

3 Sample believed to be contaminated with methylene chloride

4 Questionable results

5 Specific organic analyses focused on priority pollutants. A few non-priority compounds were detected by the procedure and were quantified; however, no effort was made to identify all non-priority pollutants.

6 Removal attributable only to the unit process

ND - Not Detected at detection limit of 0.01 mg/1

TABLE 16. ISOTHERM SORPTION DATA ON GROUNDWATER FROM WELLS OW9 AND W17d

		OW9 Groundwater (1)								W17d Groundwater (2)								
SORBENT	DOSE	TOC		TOC SORBED				TOC REMOVAL		DOSE	TOC		TOC SORBED				TOC REMOVAL	
		C_f (mg/l)		X(mg/l)		X/M(mg/g)		(%)			C_f (mg/l)		X(mg/l)		X/M(mg/g)		(%)	
	(g/l)	pH 9.4	pH 7.0	pH 9.4	pH 7.0	pH 9.4	pH 7.0	pH 9.4	pH 7.0	(g/l)	pH 9.4	pH 7.0	pH 9.4	pH 7.0	pH 9.4	pH 7.0	pH 9.4	pH 7.0
BLANK	0	1820	1820							0	230	220						
PS 300	5	1647	1590	173	230	34.6	46.0	9.5	12.6	0.5	150	138	80	82	160	164	34.8	37.3
	10	1518	1532	302	288	30.2	28.8	16.6	15.8	5	36	30	194	190	38.8	38.0	84.3	86.4
	50	1273	1244	547	567	10.9	11.5	30.0	31.6	50	10	10	220	210	4.4	4.2	95.6	95.4
	100	1115	1158	705	662	7.0	6.6	38.7	36.4									
Nuchar S-A	5	1619	1619	201	201	40.2	40.2	11.0	11.0	0.5	135	124	95	96	190	192	41.3	43.6
	10	1619	1547	201	273	20.1	27.3	11.0	15.0	5	40	32	190	188	38.0	37.6	82.6	85.4
	50	1359	1330	461	490	9.2	9.8	25.3	26.9	50	13	13	217	207	4.3	4.1	94.3	94.1
	100	1187	1216	633	604	6.3	6.0	34.8	33.2									
HDC	5	1705	1705	115	115	23.0	23.0	6.3	6.3	0.5	178	178	52	42	104	84.0	22.6	19.1
	10	1676	1647	144	173	14.4	17.3	7.9	9.5	5	42	38	188	182	37.6	36.4	81.7	82.7
	50	1388	1417	432	403	8.6	8.1	23.7	22.1	50	9	10	221	210	4.4	4.2	96.1	95.4
	100	1230	1187	590	633	5.9	6.3	32.4	34.8									
XE-340	100	1475	1532	345	288	3.4	2.9	19.0	15.8	5	181	167	49	53	9.8	10.6	21.3	24.1
XE-347	100	1302	1187	518	633	5.2	6.3	28.5	34.8	5	200	190	30	30	6.0	6.0	13.0	13.6
XAD-4	100	1475	1503	345	317	3.4	3.2	19.0	17.4	5	177	150	53	70	10.6	14.0	23.0	31.8

(1) Contact Time - 4 hr
(2) Contact Time - 1 hr

TABLE 17. ISOTHERM SORPTION DATA FOR OW9 AND W17d GROUNDWATERS PRETREATED BY ACTIVATED SLUDGE

Sample	TOC C_f(mg/1)	TOC Adsorbed X(mg/1)	Capacity X/M(mg/g)	TOC Removal (%)
Blank - OW9 Groundwater pretreated by activated sludge	1077	-	-	-
OW9 Groundwater pretreated by activated sludge	744	333	66.6	30.9
Blank - W17d Groundwater pretreated by activated sludge	99	-	-	-
W17d Groundwater pretreated by activated sludge	12	87	17.4	87.9

Sorbent: FS 300 Carbon

Dose: 5 g/1

Contact Time: 1 hr

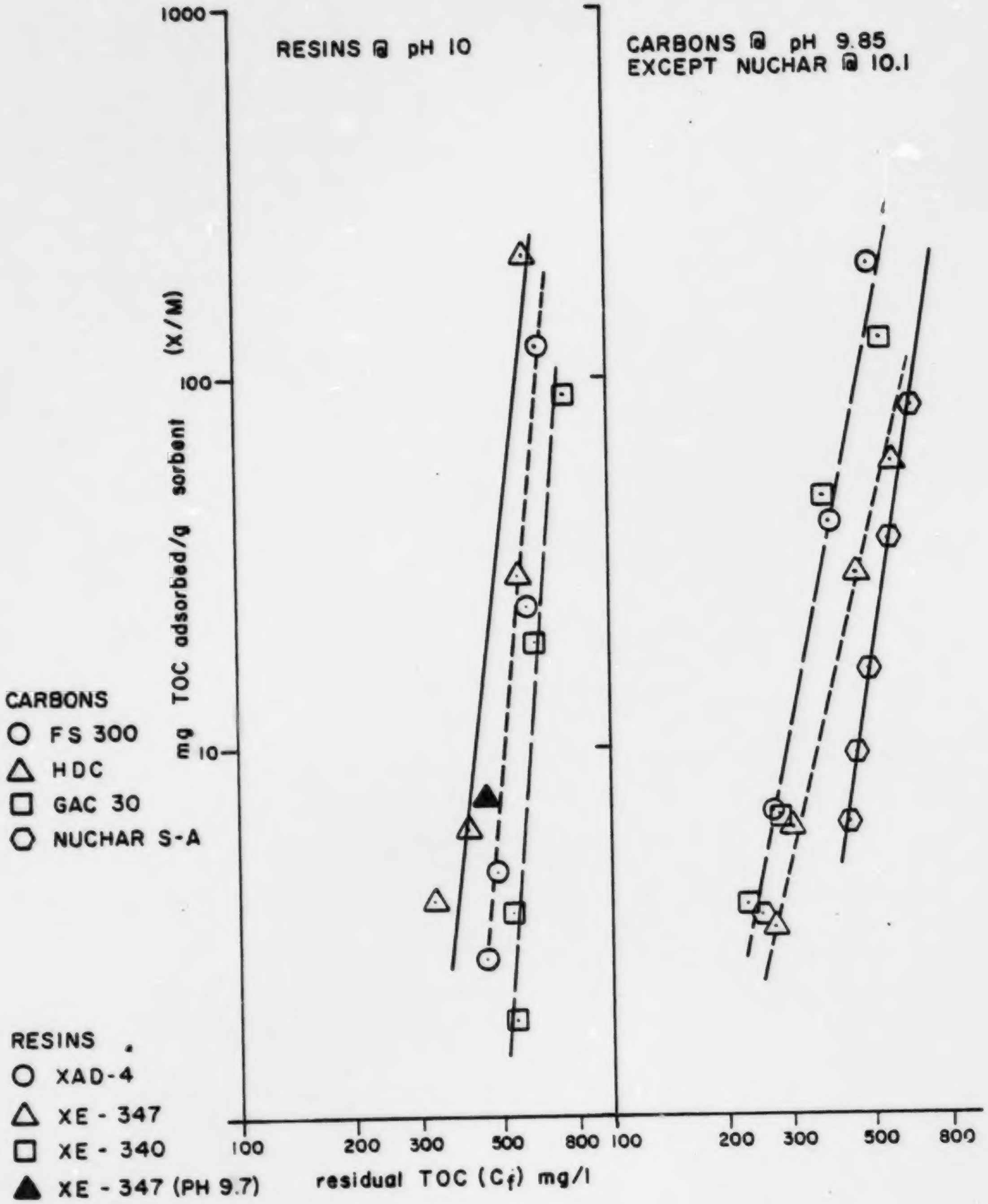


Figure 8. Adsorption Isotherms, Raw Composite Groundwater, pH 10.0 .

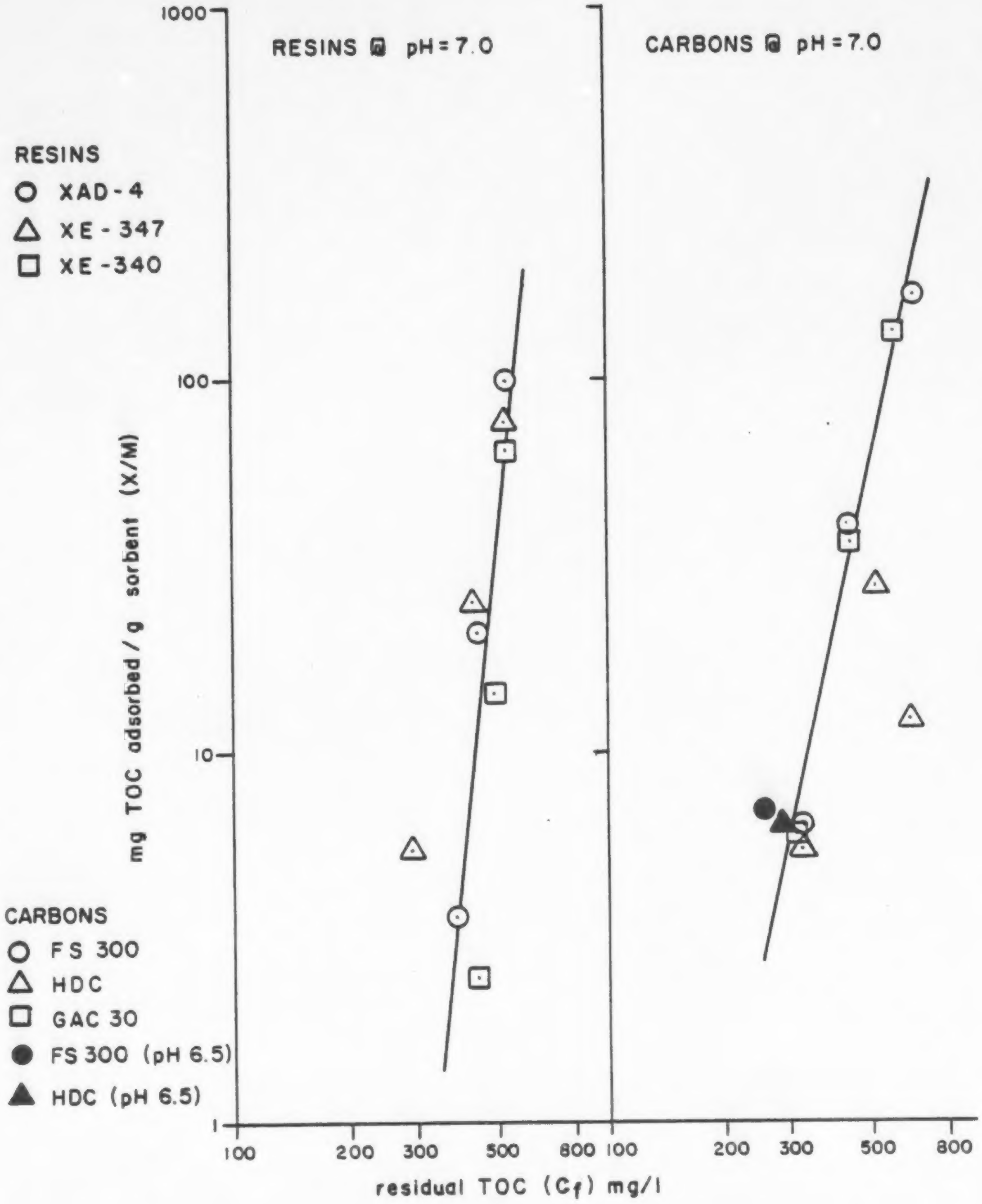


Figure 9. Adsorption Isotherms, Raw Composite Groundwater, pH 7.0.

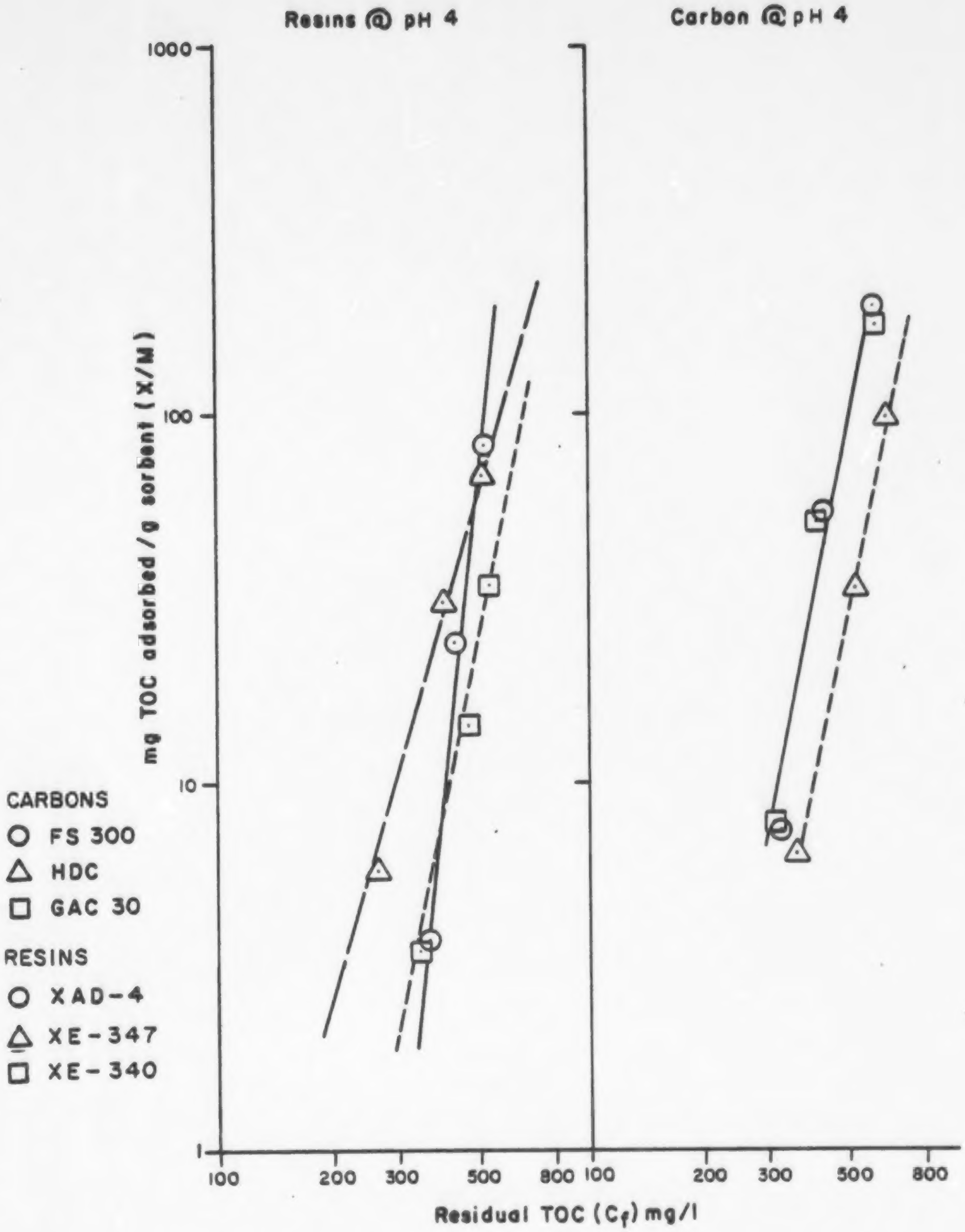


Figure 10. Adsorption Isotherms, Raw Composite Groundwater, pH 4.0.

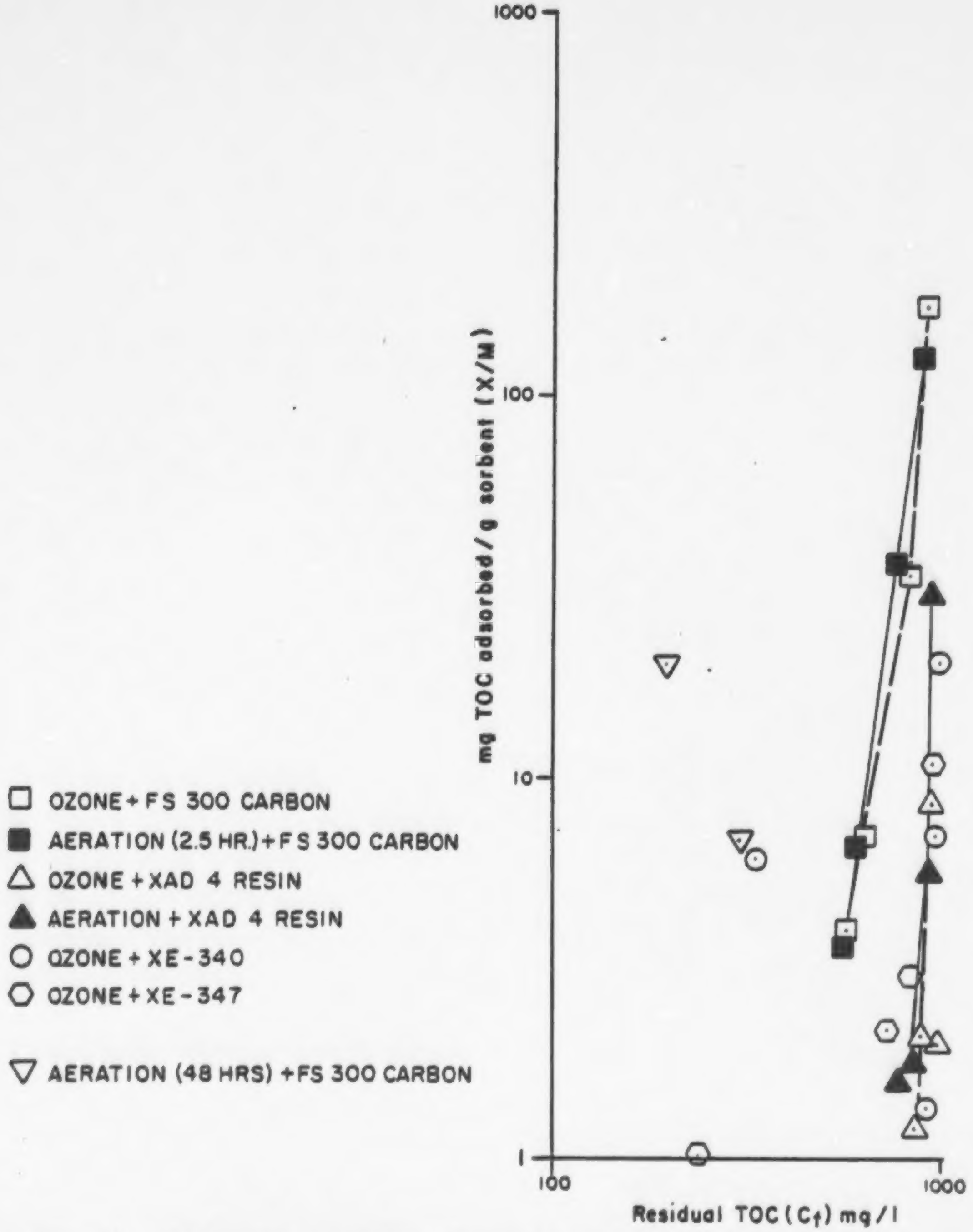


Figure 11. Adsorption Isotherms, Composite Groundwater Pretreated by Ozonation or Aeration.

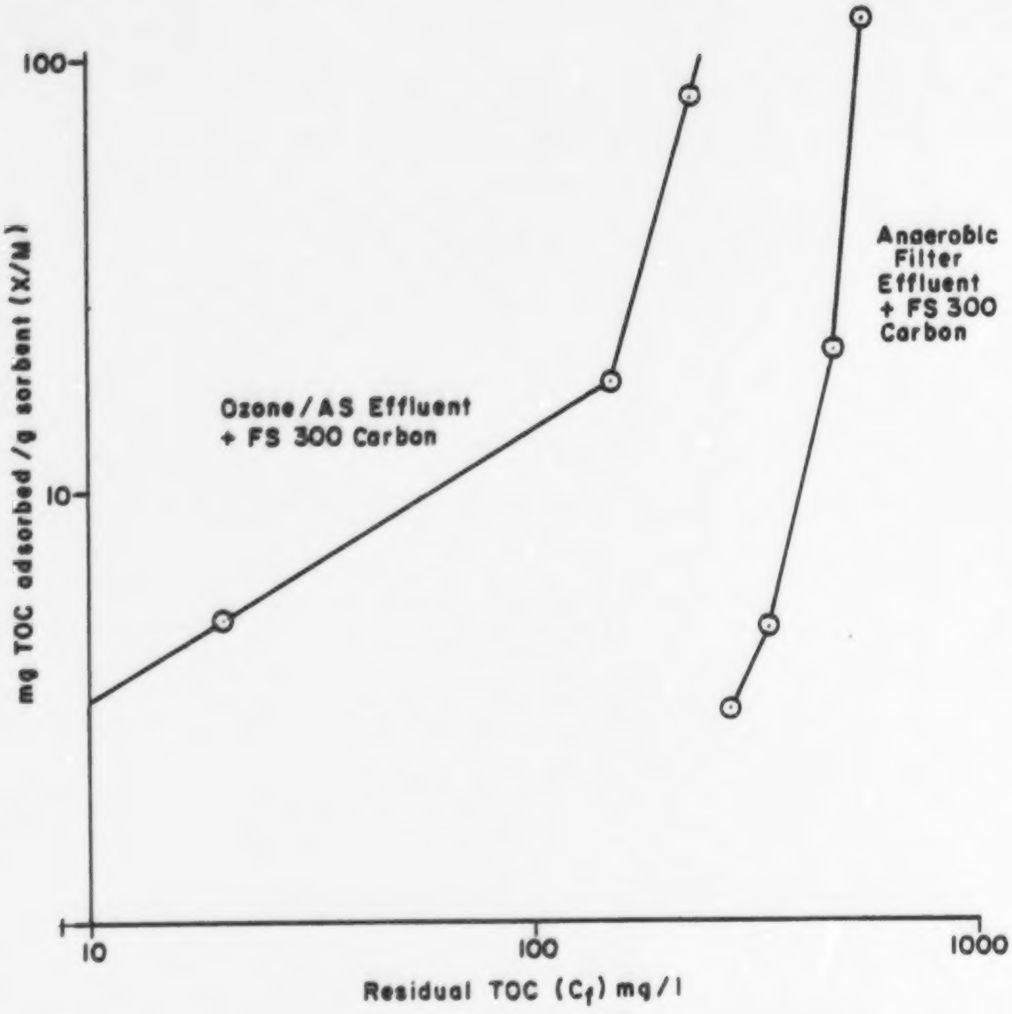


Figure 12. Adsorption Isotherms, Composite Groundwater Pretreated by Ozonation/Activated Sludge and Upflow Anaerobic Filter.

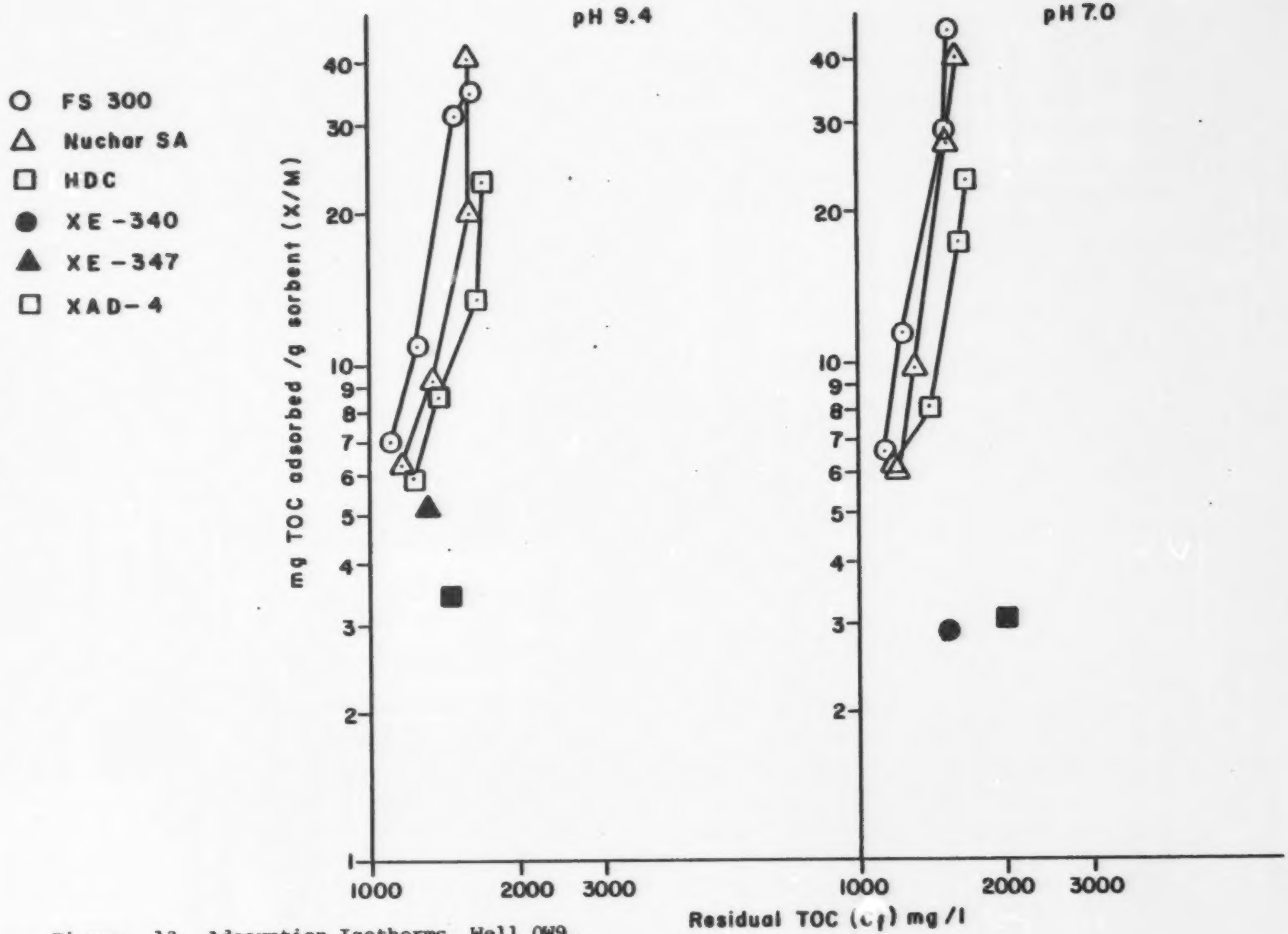


Figure 13. Adsorption Isotherms, Well OW9.

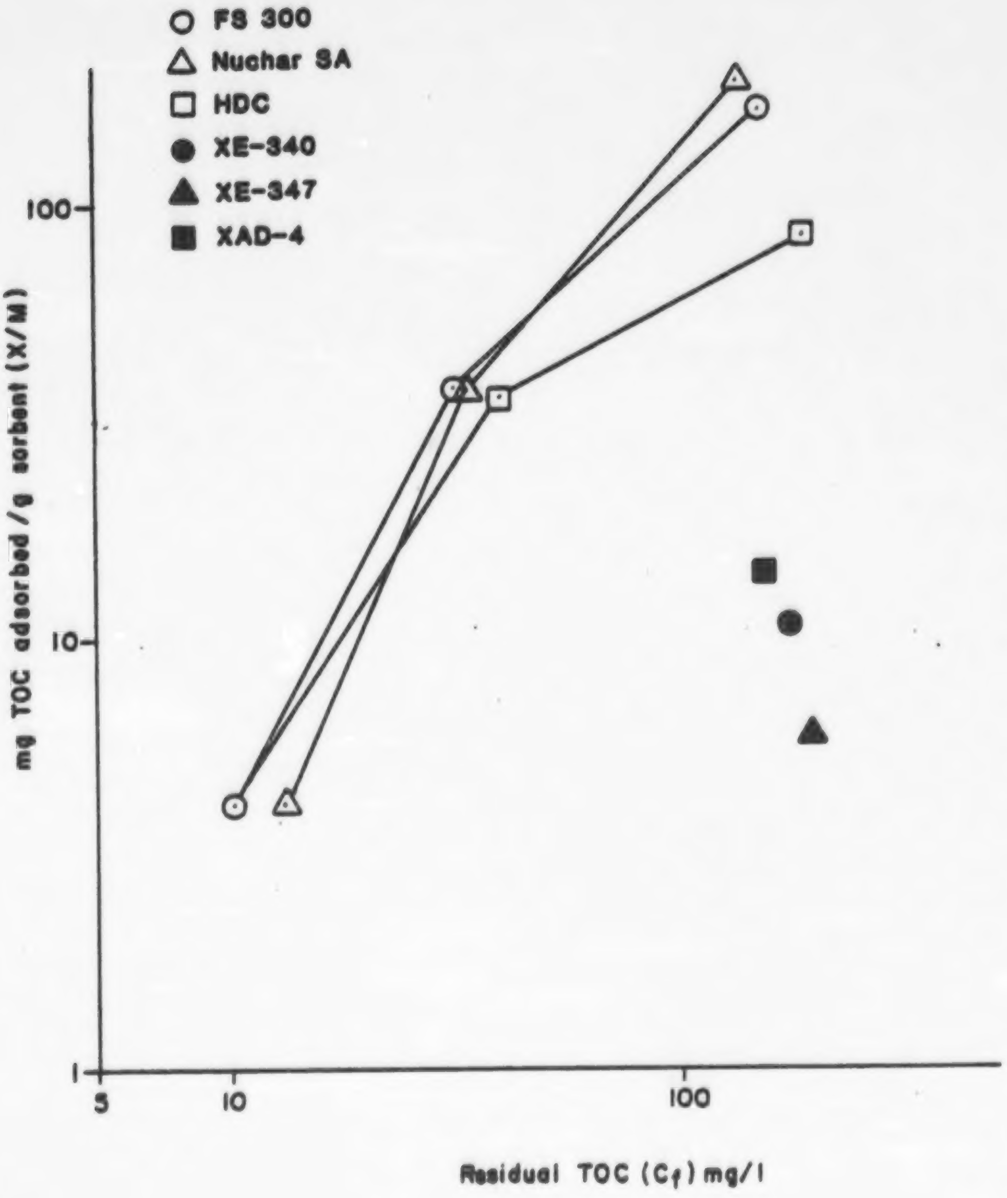


Figure 14. Adsorption Isotherms, Well W17d, pH 7.0.

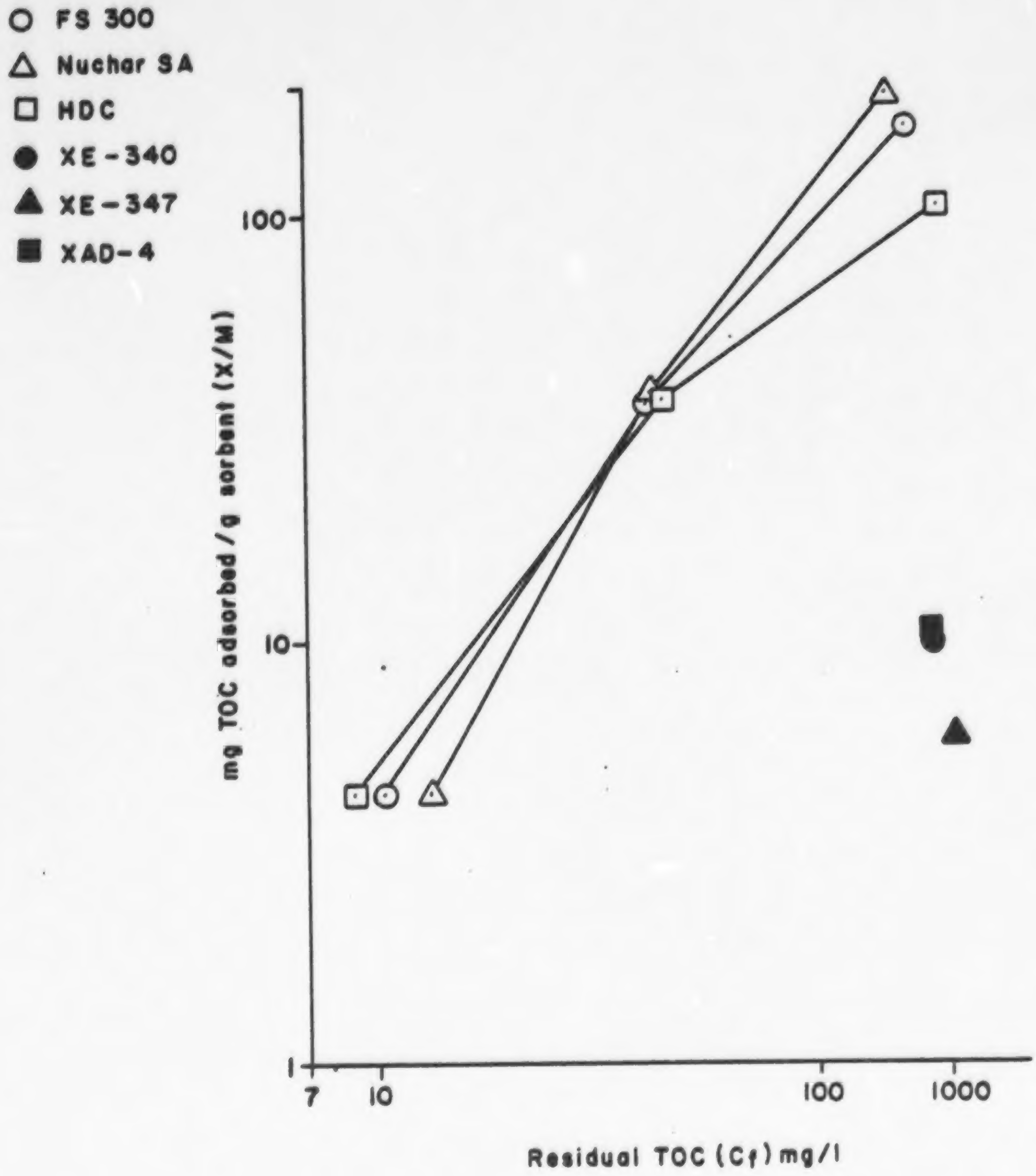


Figure 15. Adsorption Isotherms, Well 17d, pH 9.4.

and anaerobic treatment by upflow filter. Results are presented in Figures 11 and 12 and Tables 12 and 13. Operating conditions for these pretreatment processes are described in subsequent sections pertaining to the unit process.

Results of these studies indicate that, in general, Freundlich isotherms are steeply sloping straight lines when plotted on a logarithmic scale. However, pretreatment by ozonation plus activated sludge (O_3/AS) resulted in an isotherm which changes slope sharply indicating the presence of adsorbates with different sorption characteristics. Except in the case of ozonation/activated sludge pretreatment, sorption characteristics were not affected by the different pretreatment methods even though initial TOC concentrations varied considerably as a result of pretreatment. Except for the ozonation/activated sludge pretreatment case, sorbents were not capable of achieving effluent TOC concentrations of less than 290 mg/l or TOC removal efficiencies of greater than 51 percent at sorbent doses of up to 100 g/l. Where comparisons were made between carbon and resin sorbents, carbon always had better sorption capability.

Figure 16 summarizes the best activated carbon and resin sorption results from the aeration and ozonation pretreatment studies.

Sequential/Batch Studies

Prior to undertaking continuous flow column adsorption studies, the following batch sequences were examined: (1) air stripping followed by carbon sorption, (2) carbon sorption followed by air stripping, and (3) carbon sorption followed by resin sorption. Wastewater TOC concentration following these treatments remained high (greater than 189 mg/l).

Results of the sequential experiments raised questions with regard to the nature and composition of the residual TOC. Therefore, it was deemed necessary to perform some specific compound analyses to gain better insight. To extend the investigation, additional separate carbon and resin sorption and sequential air sparging-carbon sorption batch experiments were conducted. Raw wastewater and treated waters were analyzed for organic priority pollutants. Results of these studies are summarized below:

- Carbon adsorption reduced almost all organic priority pollutants to less than GC/MS detection limits. An exception was benzoic acid, which would not be expected to be removed by carbon. TOC removal capacity compared favorably with earlier results.

- Resin sorption proved to be only slightly less effective than carbon sorption. TOC removal capacity compared favorably with earlier results. Most organic priority pollutants were reduced to below detection limits. All were reduced by at least 98 percent, however, several still remained at 170 to 250 mg/l.

- Carbon treatment of air stripped groundwater generally resulted in reduction to less than detection limits for the organic priority pollutants

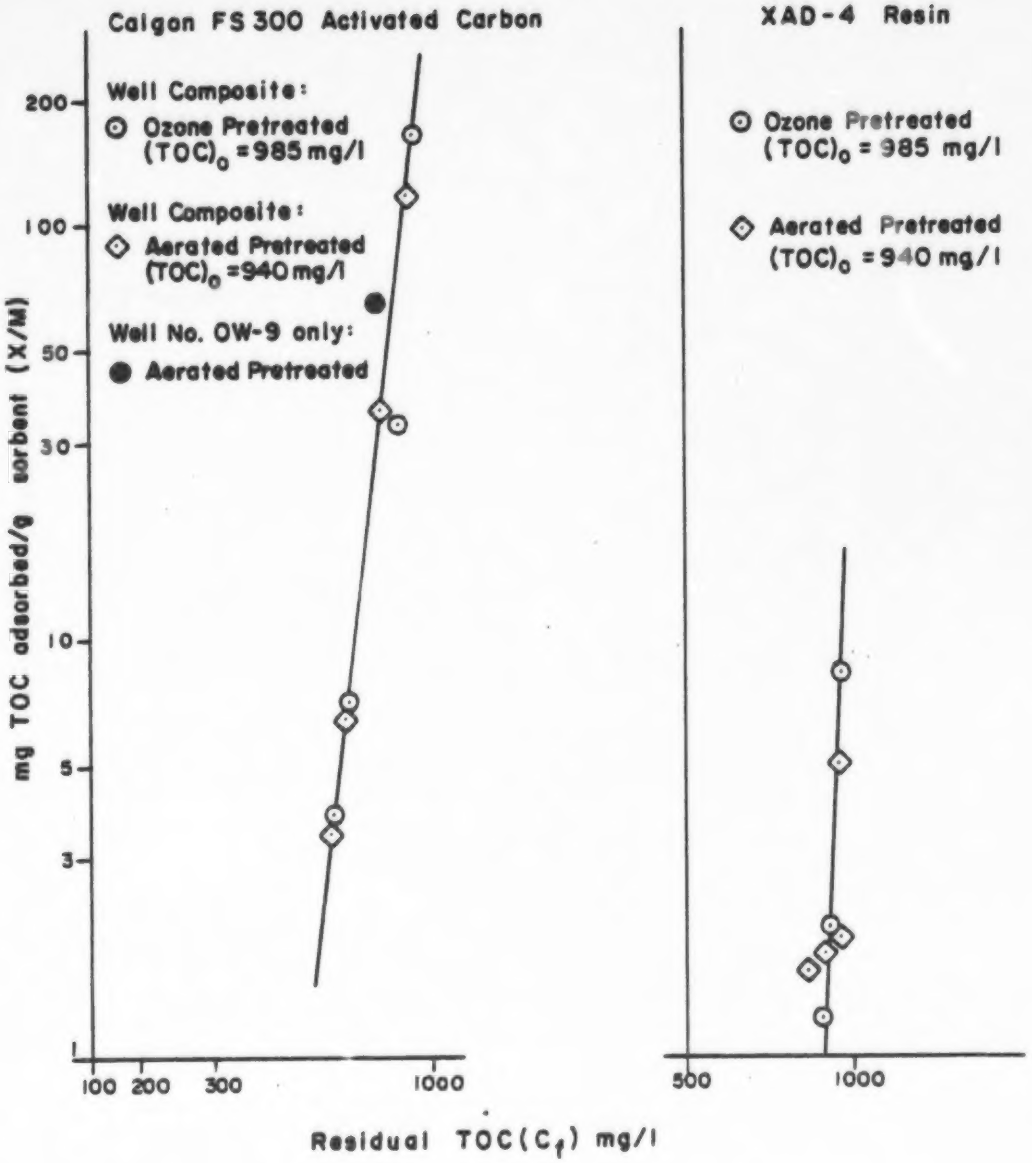


Figure 16. Adsorption Isotherms: Comparison of the Best Carbon and the Best Resin (Aerated or Ozone Pretreated).

remaining after stripping. All were reduced by more than 98 percent. TOC adsorption capacity was similar to previous tests.

- Despite good removals of organic priority pollutants, a significant residual TOC (301-455 mg/l) was measured in all treated samples. This residual represents unidentified, non-priority organic pollutants. Specific organics breaking through most consistently were 1,2-dichloroethane, benzene, dimethylaniline and camphor.

- Preaeration followed by granular activated carbon sorption appeared to be effective for the Ott/Story Site removing volatile priority pollutants, and virtually all acid and base/neutral substances. Residual TOC values remained high, however.

A limited number of isotherm adsorption studies were conducted using OW9 and W17d groundwater samples individually (See Table 16 and Figures 13, 14, and 15). The isotherms again are steeply sloping lines. Results indicate that:

- pH adjustment made very little difference in TOC adsorption with the exception that XAD-4 performed slightly better at pH 9.4.

- Carbons performed much better than resins for both waste streams and at both pH values.

- The three carbons performed similarly with FS-300 and Nuchar SA having slightly greater equilibrium adsorption capabilities.

- At the maximum dose tested, TOC removals from OW9 and W17d groundwater were 39 percent and 95 percent respectively and resulting TOCs were about 1100 mg/l and 10 mg/l, respectively.

As a result of the isotherm and sequential batch studies, it generally was concluded that adsorption is a unit process applicable to the situation at the Ott/Story Site. Carbon adsorption alone and resin sorption to a lesser extent were capable of achieving high degrees of organic priority pollutant removals. However, the adsorption process alone was not capable of reducing groundwater TOC concentrations to levels typically acceptable for direct discharge to a surface water.

Based upon the steeply sloping straight line of the adsorption isotherms, it is assumed that carbon capacity is not fully used; thus, residual organics are not sorbable. Pretreatment by various unit processes with adsorption used as a polishing process provided additional TOC removal. Results of continuous flow process trains employing adsorption in the pretreatment as well as polishing modes are presented later.

Continuous Flow Studies - -

Table 18 provides a comprehensive listing and summary of continuous flow adsorption studies. For this series of studies, adsorption was used as the primary treatment process, for pretreatment, and for post-treatment. When

TABLE 18. CONTINUOUS FLOW ADSORPTION STUDIES

CONTINUOUS FLOW STUDY NUMBER	SORBENT	WASTEWATER	HYDRAULIC LOADING RATE ($1/m^2$.min)	COLUMNS	CUMULATIVE SORBENT DEPTH (cm)	EMPTY BED CONTACT TIME (min)	BED VOLUMES PROCESSED	COMMENTS
1	FS 300	raw composite (OW9 and W17d)	81	1	90	11	351	See Figure 17
				2	180	22	175	
				3	270	33	117	
				4	360	44	88	
2	FS 300	raw composite (OW9 and W17d)	81	1	90	11	248	See Figure 19
				2	180	22	124	
				3	270	33	83	
				4	360	44	62	
3	FS 300	raw composite (OW9 and W17d)	81	1	90	11	503	See Figures 18, 20 and Table 19; activated sludge used as post-treatment
				2	180	22	251	
				3	270	33	168	
4	FS 300	raw composite (OW9 and W17d)	81	1	90	11	625	See Figures 18 and 20; activated sludge used as post-treatment
				2	180	22	312	
				3	270	33	208	
5	XE-347	raw composite (OW9 and W17d)	81	1	48.3	6	121	
				2	104.2	13	56	
				3	156.3	20	38	
6	XE-347	raw composite (OW9 and W17d)	81	1	50	6	106	See Figure 19
				2	100	13	53	
				3	150	20	35	

(Continued)

TABLE 18. (Continued)

CONTINUOUS FLOW STUDY NUMBER	SORBENT	WASTEWATER	HYDRAULIC LOADING RATE ($1/m^2.min$)	COLUMNS	CUMULATIVE SORBENT DEPTH (cm)	EMPTY BED CONTACT TIME (min)	BED VOLUMES PROCESSED	COMMENTS
7	FS 300	raw composite (OW9 and W17d)	81.6	1 2 3	93 183.5 272	11 22 33	121 61 41	Activated sludge used as post-treatment
8	FS 300	raw composite (OW9 and W17d)	3.35-4.33	1	89	226	210	See Figure 20; Activated sludge used for post-treatment
9	FS 300	raw composite (OW9 and W17d)	2.96-5.10	1	84	213	220	See Figure 20; Activated sludge used for post-treatment
10	FS 300	raw composite (OW9 and W17d)	3.74-4.73	1	88	223	197	Activated sludge used for post-treatment
11	FS 300	composite (OW9 and W17d) pretreated by ozonation	1.57-1.96	1	81.5	458	101	See Figure 20; activated sludge used for post-treatment after adsorption
12	FS 300	composite (OW9 and W17d) pretreated by ozonation and activated sludge	1.96-2.21	1	30	143	76	See Figure 20
13	FS 300	composite (OW9 and W17d) pretreated by activated sludge	82	1	79	10	100	See Figure 20

(Continued)

TABLE 18. (Continued)

CONTINUOUS FLOW STUDY NUMBER	SORBENT	WASTEWATER	HYDRAULIC LOADING RATE (l/m^2.min)	COLUMNS	CUMULATIVE SORBENT DEPTH (cm)	EMPTY BED CONTACT TIME (min)	BED VOLUMES PROCESSED	COMMENTS
14	FS 300	OW9 Groundwater	2.82-4.11	1	80	240	82	See Figure 22; Activated sludge used for post-treatment
15	FS 300	OW9 Groundwater	2.77-3.75	1	97	296	63	See Figure 22; Activated sludge used for post-treatment
16	FS 300	raw composite (OW9 and W17d)	1.96-3.92	1	68.5	203	65	Upflow anaerobic filter then activated sludge used for post-treatment
17	FS 300	raw composite (OW9 and W17d)	2.56-4.53	1	78.5	235	34	Upflow anaerobic filter then activated sludge used for post-treatment
18	FS 300	W17d groundwater	81.6	1 2	85 167	11 21	122 56	See Figure 22
19	FS 300	OW9 groundwater	3.55-4.44	1	69	182	23	See Figure 22; upflow anaerobic filter used for post-treatment

used as the primary process, three or four carbon columns were arranged in series and operated at a constant hydraulic loading rate of about 2 gpm/ft^2. (See Table 2 for SI conversion). When used as part of a continuous process train, a single carbon column operated at a loading rate dictated by the other unit operations was used. Based upon results of the isotherm studies, FS-300 granular activated carbon (GAC) and XE-347 carbonaceous resin were selected as sorbents to be further investigated throughout the continuous flow study phase.

During the course of conducting the studies listed on Table 18, it was noted that TOC rapidly broke through the adsorption system; this is illustrated on Figures 17, 18, and 19. Effluent TOC values of less than about 100 mg/l could be achieved only within the first three to ten bed volumes of loading. Removal efficiency decreased rapidly to less than 50 percent. Therefore, with influent TOC ranging from 600 to 1000 mg/l (in the composite of OW9 and W17d), an effluent TOC of 300 to 500 mg/l was typical after a short period of operation.

Figure 17 illustrates the progression of TOC breakthrough through a system with four columns in series. These results are typical of the adsorption process in general and of other studies conducted during investigations at the Ott/Story site.

Figures 19, 20, and 21 illustrate TOC adsorption by GAC and XE-347 resin for selected studies under different conditions as summarized in Table 18. These data indicate that:

- Operating at empty bed contact times (EBCT) from 10 to 226 min had no consistent effect on the adsorption of TOC. This also is demonstrated by the results of studies with two columns in series (Figure 19) and three columns in series (Figure 20, 21). In these studies, the equilibrium weight of TOC adsorbed per unit weight of carbon in the first column (having an EBCT of 11 min) of the series was equivalent to the adsorption of the entire bed (having an EBCT of 22 min for two columns and 33 min for three columns) at any point along the carbon loading curve.

- The adsorption capacity of XE-347 was lower than that of FS-300 under similar study conditions. Adsorption capacity of FS-300 and typical TOC breakthrough characteristics were not affected by pretreating the wastewater with ozone.

- Carbon adsorption capacity appeared to be slightly improved by pretreating with a process train consisting of ozonation followed by activated sludge. However, improvement in capacity was only slightly better than demonstrated by activated sludge pretreatment alone.

Despite the inability to maintain high levels of TOC removal, GAC adsorption demonstrated substantial organic priority pollutant removals. As indicated on Table 19, even when loaded at 111 mg TOC/g carbon, FS-300 continued to sustain high levels (83 percent or better) of priority pollutants removal at TOC removals of only 35 percent and effluent TOC concentrations of greater

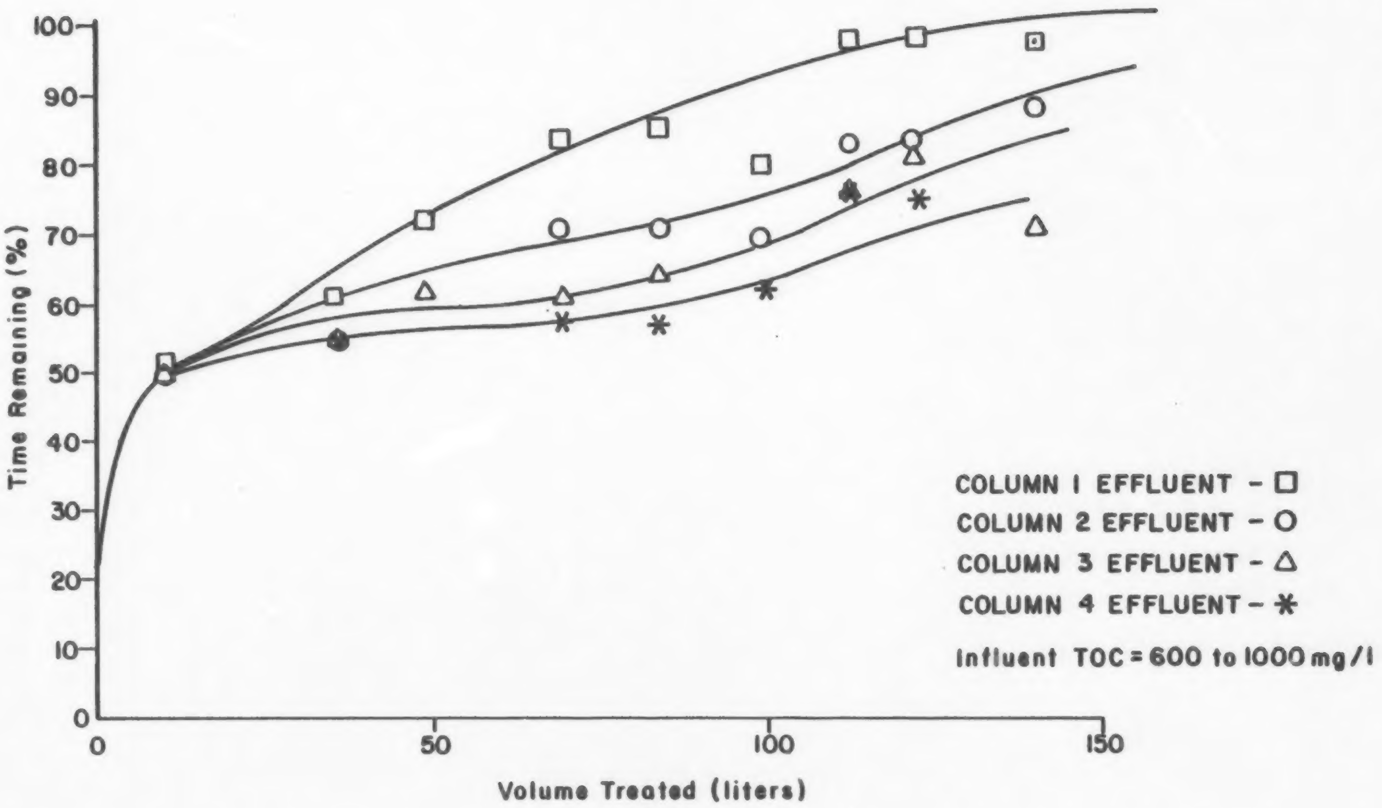


Figure 17. Typical TOC Performance (Breakthrough) Curve.

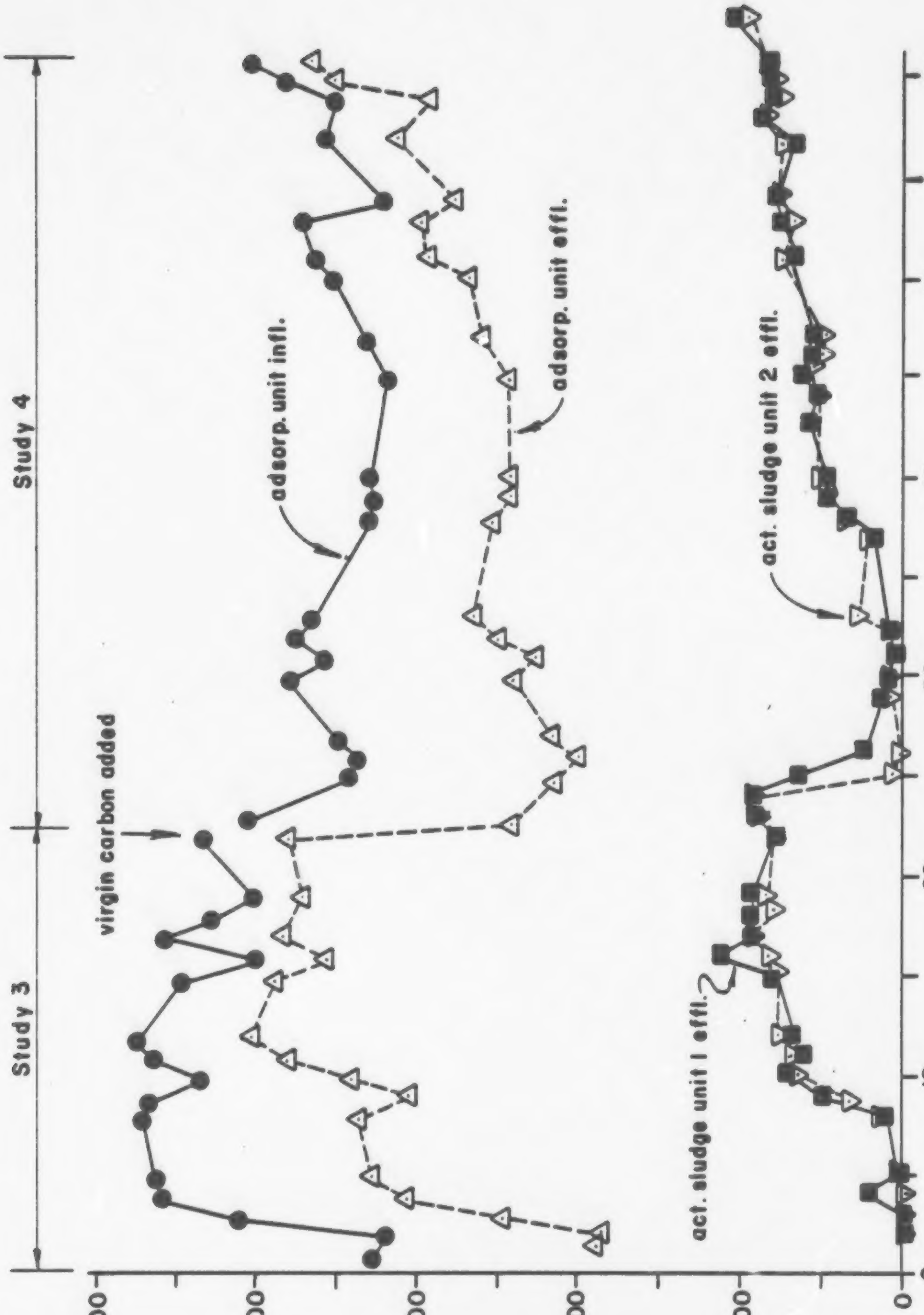


Figure 18. Performance of GAC/Activated Sludge Process.

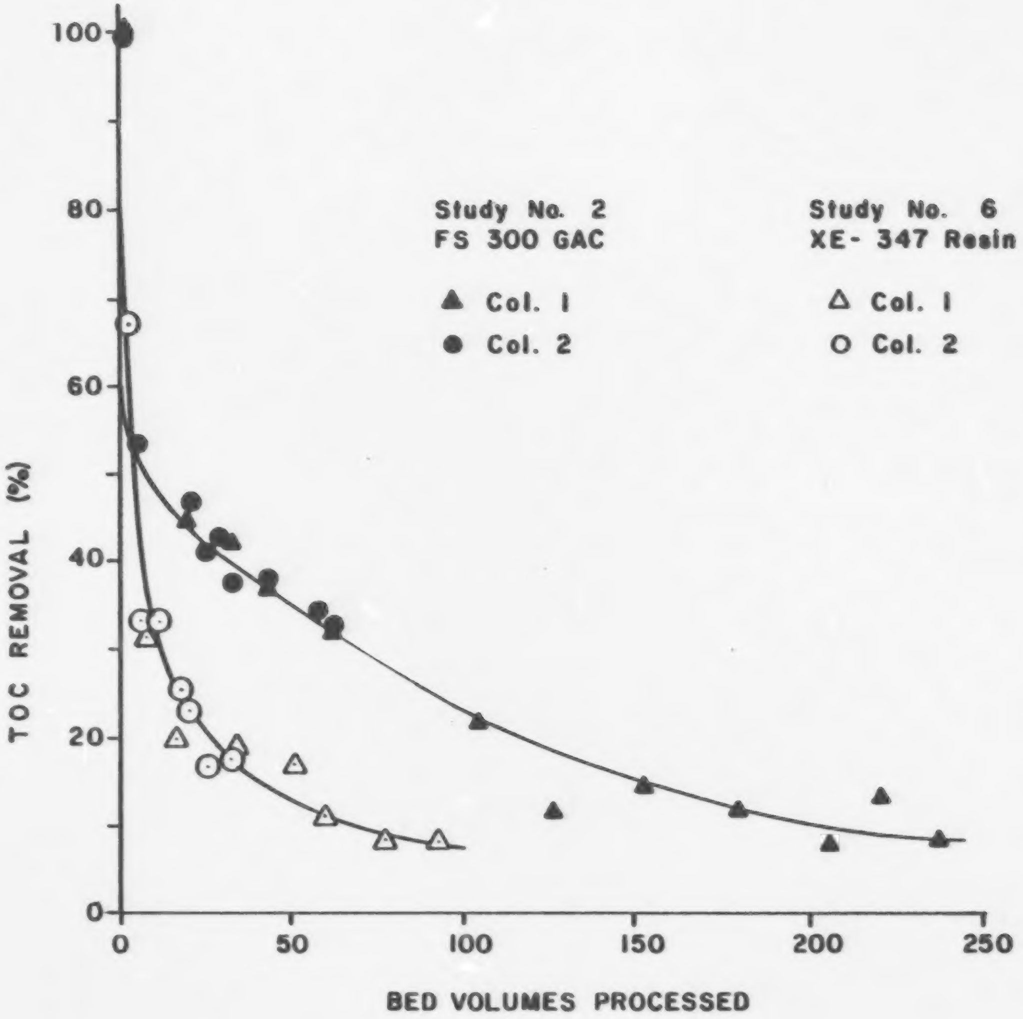
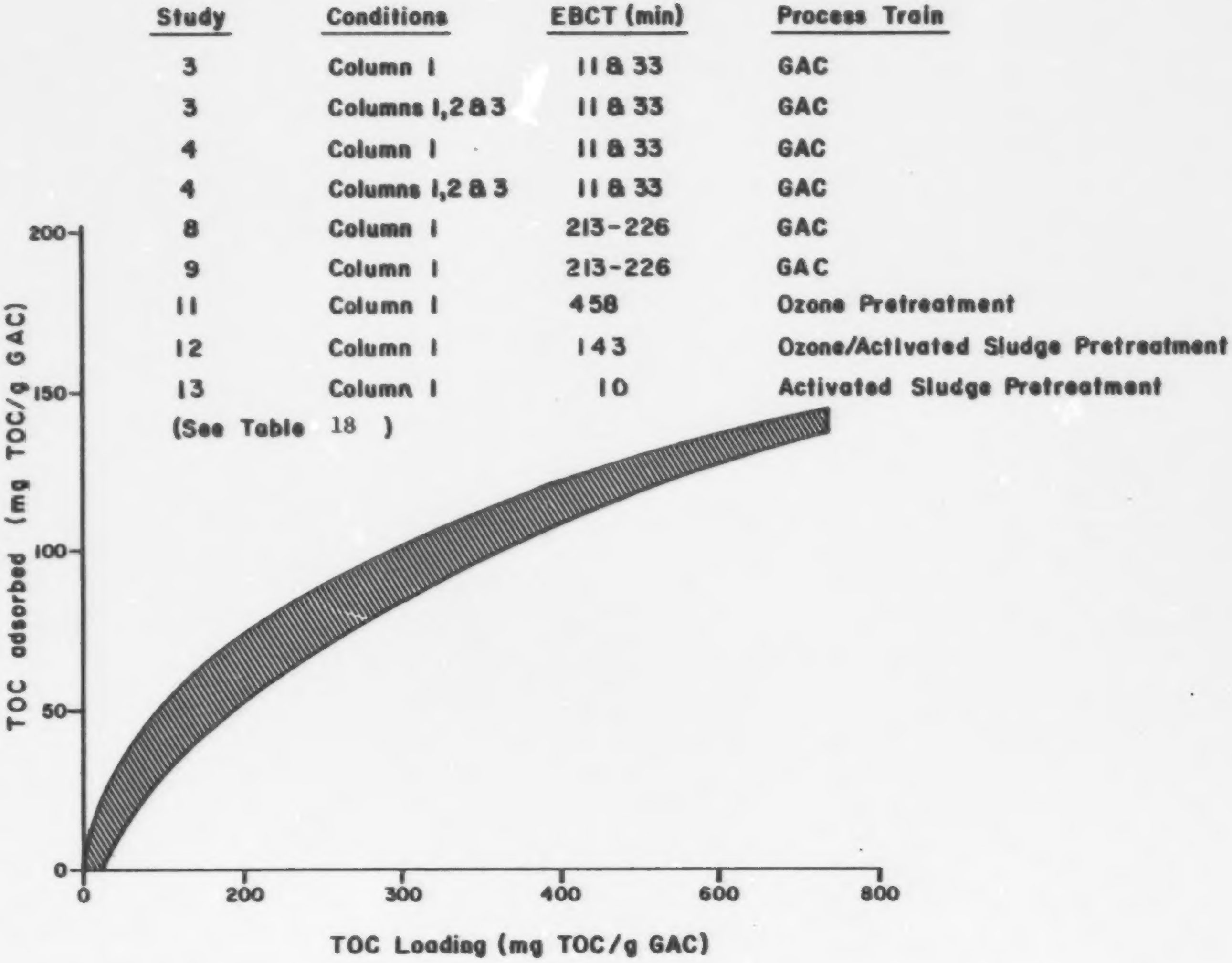


Figure 19. Comparison Between Carbon and Resin Adsorption.



Study	Conditions	EBCT (min)	Process Train
3	Column I	11 & 33	GAC
3	Columns I,2 & 3	11 & 33	GAC
4	Column I	11 & 33	GAC
4	Columns I,2 & 3	11 & 33	GAC
8	Column I	213-226	GAC
9	Column I	213-226	GAC
11	Column I	458	Ozone Pretreatment
12	Column I	143	Ozone/Activated Sludge Pretreatment
13	Column I	10	Activated Sludge Pretreatment

(See Table 18)

Figure 20. TOC Adsorption by Granular Activated Carbon.

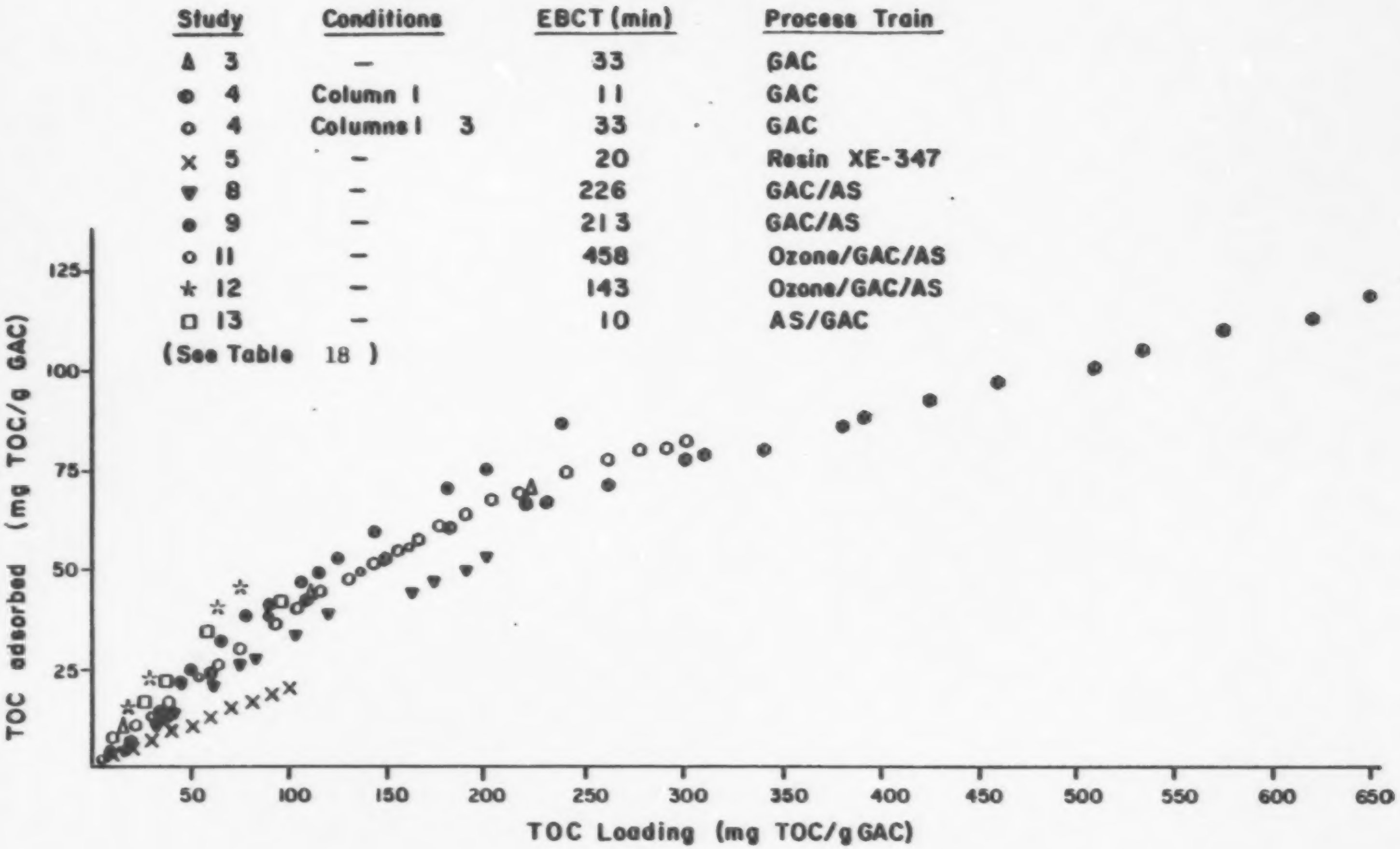


Figure 21. TOC Adsorption by Granular Activated Carbon.

TABLE 19. TOC AND PRIORITY POLLUTANT DATA FOR GRANULAR ACTIVATED CARBON/ACTIVATED SLUDGE PROCESS TRAIN

	Collected on Day 2*		Collect on Days 9 and 10*			Collected on Day 17*	
	Raw Ground-water	GAC Effl.	Raw Ground-water	GAC Effl.	AS Effl.	GAC Effl.	AS Effl.
Average carbon loading when sample collected (mg TOC/g Carbon)		19		111		233	
Parameter (mg/1):							
TOC	637	380	929	604	90	770	183
Total Cyanide	NA	NA	0.11	0.21	0.23	0.23	0.20
CN_A	NA	NA	<0.05	<0.05	<0.05	<0.05	<0.05
Total Phenol	NA	NA	16	<0.16	<0.10	<0.10	<0.10
Methylene chloride	2.1	0.029	14	0.01	ND	0.16	ND
1,1-Dichloroethene	1.6	ND	0.06	0.01	ND	ND	ND
1,1-Dichloroethane	2.4	ND	0.17	0.02	ND	ND	ND
Trans-1,2-dichloroethane	0.06	ND	0.04	ND	ND	ND	ND
Chloroform	9.8	ND	0.70	0.06	ND	ND	ND
1,2-Dichloroethane	72	ND	25	1.4	ND	ND	ND
1,1,1-Trichloroethane	7.6	ND	0.39	0.04	ND	0.05	ND
Trichloroethylene	0.06	ND	0.03	ND	ND	ND	ND
Benzene	1.2	ND	1.5	0.02	ND	ND	ND
1,1,2-Trichloroethane	0.11	ND	0.07	ND	ND	ND	ND

(Continued)

TABLE 19. (Continued)

	Collected on Day 2*		Collect on Days 9 and 10*			Collected on Day 17*	
	Raw Ground-water	GAC Effl.	Raw Ground-water	GAC Effl.	AS Effl.	GAC Effl.	AS Effl.
Perchloroethylene	0.49	ND	1.9	ND	ND	ND	ND
Toluene	2.3	ND	0.97	0.05	ND	0.01	ND
Chlorobenzene	0.23	ND	0.29	ND	ND	ND	ND
Phenol	0.025	ND	0.028	ND	ND	ND	ND
2-Chlorophenol	0.040	ND	0.036	ND	ND	ND	ND
2,4-Dichlorophenol	0.010	ND	0.010	ND	ND	ND	ND
1,2-Dichlorobenzene	0.085	ND	0.077	ND	ND	ND	ND
Dibutyl phthalate	ND	ND	ND	ND	0.05	ND	ND

NA - Not Analyzed
ND - Not Detected
No other priority pollutants detected at 0.01 mg/l detection limit
* - Refers to Adsorption Study No.3 as illustrated on Figure 18

than 600 mg/l. At 71 bed volumes, representing a loading of 233 mg TOC/g carbon, the only priority pollutants detected in the GAC effluent were methylene chloride, 1, 2-dichloroethane, and toluene.

The significant differences in the adsorption characteristics of groundwaters from two different wells at the Ott/Story site are illustrated in Figure 22. Organic materials in W17d, as measured by TOC concentration, were more readily sorbed by FS 300 than was TOC in W17d. Moreover, the sorption characteristics of OW9 were comparable to the OW9/W17d composite, indicating that some compounds in either OW9 or W17d are preferentially adsorbed to the exclusion of other compounds despite the fact that sufficient opportunities for adsorption still exist.

During the course of the continuous flow adsorption studies, results were found to correlate well with isotherm data previously presented. Moreover, priority pollutant removals were in agreement with other published data summarized in an earlier project report (1).

Biological Treatment Activated Sludge

A number of activated sludge treatability studies were conducted. These included use of a biomass acclimated to raw contaminated groundwater, sludge seeded with Phenobac®, addition of powdered activated carbon to the activated sludge aeration chamber, and pretreatment of the groundwater by carbon adsorption or ozonation. Table 20 summarizes the operating conditions and results of these studies. Time was allowed between studies for acclimation to new study conditions.

Several attempts were made to acclimate an activated sludge culture to the raw groundwater. Mixed liquor, obtained from the preaeration basin of the Muskegon County wastewater treatment plant, was fed a mixture of raw municipal wastewater and groundwater. Over the course of about nine weeks, the fraction of groundwater in the feed was increased from 0 to 100 percent in approximately 10 percent increments. Hydraulic retention time in the aeration chamber was about seven hours and mixed liquor suspended solids averaged about 3800 mg/l during this period. To assure adequate nutrients, phosphorus, as phosphoric acid, was added to provide a TOC:N:P ratio of about 100:17:5. Hydrochloric acid or sodium hydroxide were used to keep the pH in the range 6.5 - 7. Daily pH adjustment was needed due to the high alkalinity and buffering capacity of the water.

Attempts to develop an acclimated culture were minimally successful. As system influent contained a greater fraction of groundwater, slight loading fluctuations resulted in growth of a poorly settling, light colored, filamentous biomass. As shown on Figure 23, once the systems were acclimated to the extent possible, TOC removal ranged from about 35 to 60 percent. Effluent TOC concentrations ranged from 174 to 472 mg/l as shown in Figure 24. However, subsequent studies indicated that the stripping effect of diffused aeration could account for about two-thirds of the removal. Performance (TOC removal) at retention times of 4.3 to 8.3 hr and about 16 hr did not appear to be significantly different.

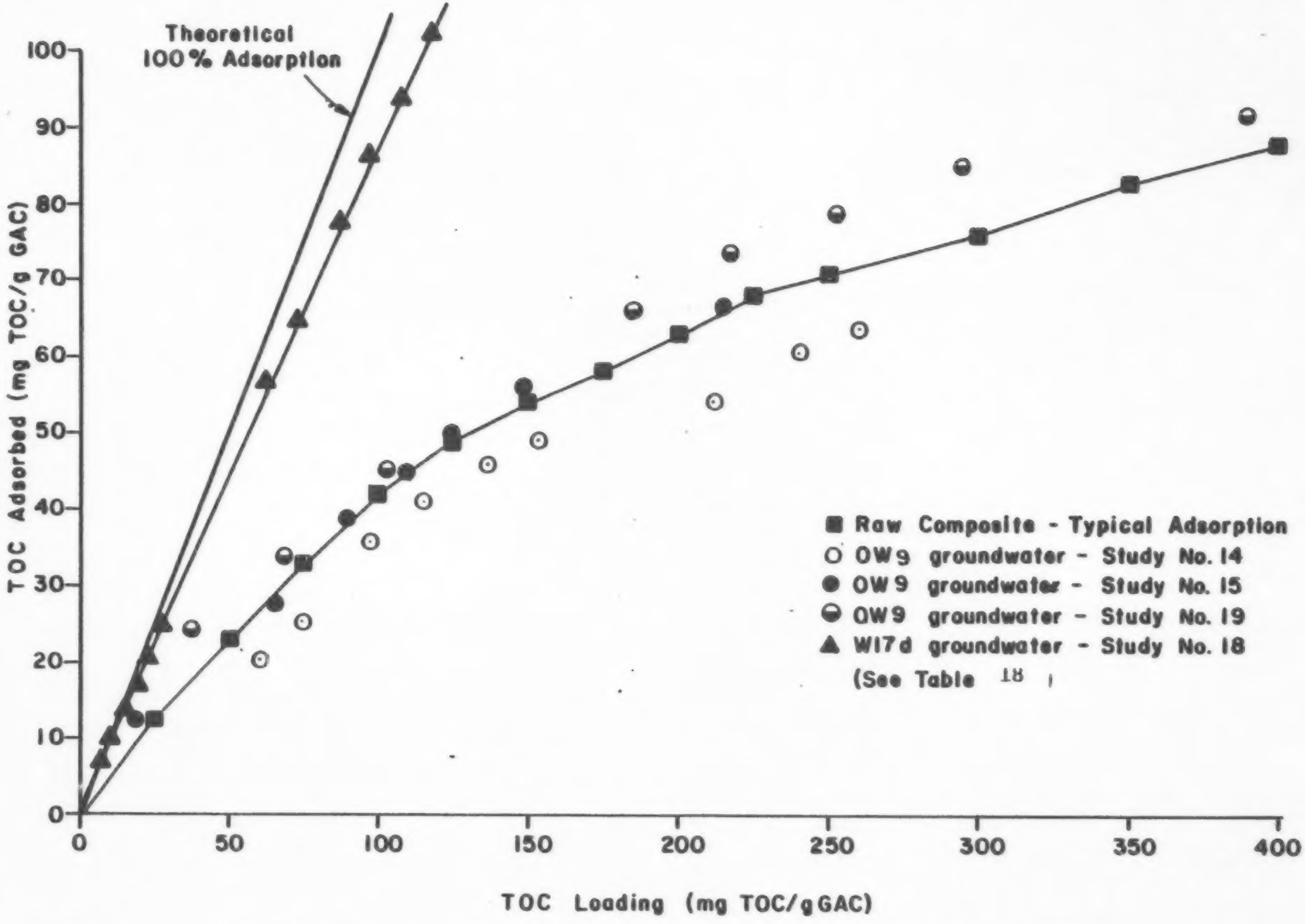


Figure 22. TOC Adsorption by GAC for Composite Groundwater and Individual Wells.

TABLE 20. STUDIES OF THE ACTIVATED SLUDGE PROCESS

		OPERATING CONDITIONS						REMOVAL			
STUDY NO.	WASTEWATER	REACTOR TYPE	HRT (hr)		TOC LOADING			No. of Data Points	TOC REMOVAL		COMMENTS
			AVER	RANGE	mg/l AVER	Lb/1000cu.ft./day AVER	RANGE		AVER	RANGE	
1	raw composite (OW9 and W17d)	R	4.6	3.0-9.8	651	209	134-301	20	50	40-57	
2	raw composite (OW9 and W17d)	R	4.3	3.6-4.4	643	217	135-280	6	47	42-57	
3	raw composite (OW9 and W17d)	R	4.6	4.0-6.2	622	208	134-236	8	37	30-40	
4	raw composite (OW9 and W17d)	S	6.0	5.0-7.9	533	135	96-205	26	54	35-69	
5	raw composite (OW9 and W17d)	S	6.1	4.3-8.0	538	127	80-205	22	51	41-68	
6	raw composite (OW9 and W17d)	S	6.9	3.3-14.6	543	157	45-279	11	43	25-64	
7	raw composite (OW9 and W17d)	R	8.3	6.9-10.4	634	114	94-145	6	46	42-49	
8	raw composite (OW9 and W17d)	R	15.6	10.8-18.2	611	62	52-79	7	61	52-68	
9	raw composite (OW9 and W17d)	R	16.1	13.9-17.8	664	62	53-76	8	63	59-70	
10	raw composite (OW9 and W17d)	R	4.3	3.4-5.2	645	228	184-266	5	42	35-49	Trace elements added
11	raw composite (OW9 and W17d)	S	5.7	1.3-9.7	517	156	74-625	28	48	37-58	Phenobac® culture
12	composite (OW9 and W17d) GAC pretreated	S	4.3	3.0-5.6	212	68	43-83	7	90	78-95	Effluent from GAC Study 2
13	composite (OW9 and W17d) GAC pretreated	S	4.8	3.4-5.6	201	69	37-94	7	90	77-100	Effluent from GAC Study 2
14	composite (OW9 and W17d) GAC pretreated	S	5.0	4.5-6.0	392	119	41-156	6	88	72-98	Effluent from GAC Study 2
15	composite (OW9 and W17d) GAC pretreated	R	6.2	5.6-6.4	489	124	63-185	10	87	61-100	Effluent from GAC Study 3
16	composite (OW9 and W17d) GAC pretreated	R	6.1	5.3-7.3	489	128	55-196	10	85	61-100	Effluent from GAC Study 3, PAC in aeration chamber
17	composite (OW9 and W17d) GAC pretreated	R	8.0	7.0-9.3	647	122	97-143	7	74	65-79	Effluent from GAC Study 3
18	composite (OW9 and W17d) GAC pretreated	R	8.2	7.3-10.4	647	120	94-137	7	71	65-74	Effluent from GAC Study 3, PAC residual in aeration chamber

(Continued)

TABLE 20. (Continued)

STUDY NO.	WASTEWATER	OPERATING CONDITIONS							REMOVAL		COMMENTS
		REACTOR TYPE	HRT (hr)		TOC LOADING			No. of Data Points	TOC REMOVAL		
			AVER	RANGE	mg/l AVER	Lb/1000cu.ft./day AVER	RANGE		AVER	RANGE	
19	composite (OW9 and W17d) GAC pretreated	R	5.9	5.6-11.1	370	92	39-121	13	87	62-100	Effluent from GAC Study 4
20	composite (OW9 and W17d) GAC pretreated	R	16.7	9.8-23.9	402	43	14-72	20	76	58-99	Effluent from GAC Study 4
21	composite (OW9 and W17d) GAC pretreated	R	6.0	5.6-8.4	465	107	66-146	14	69	53-81	Effluent from GAC Study 4
22	composite (OW9 and W17d) GAC pretreated	R	6.6	5.1-7.0	450	107	66-146	8	59	53-72	Effluent from GAC Study 4
23	composite (OW9 and W17d) resin pretreated	R	4.0	3.9, 4.0	520	197	152-243	2	79	74, 82	Effluent from resin Study 5
24	composite (OW9 and W17d) resin pretreated	R	8.8	7.3,10.4	520	87	83-91	2	80	73, 83	Effluent from resin Study 5
25	composite (OW9 and W17d) resin pretreated	R	4.5	4.4, 4.6	405	160	94-226	2	68	54, 74	Effluent from resin Study 6
26	composite (OW9 and W17d) resin pretreated	R	9.5	8.8,11.5	538	86	47-119	3	72	53, 79	Effluent from resin Study 6
27	composite (OW9 and W17d) GAC pretreated	R	7.7	6.2-9.8	319	63	33-116	10	93	47-100	Effluent from GAC Study 7
28	composite (OW9 and W17d) GAC pretreated	R	8.6	7.6-8.9	379	66	56-89	9	83	76-88	Effluent from GAC Study 7
29	composite (OW9 and W17d) GAC pretreated	R	8.6	7.6-9.8	490	85	38-123	22	76	54-100	Effluent from GAC Study 8
30	composite (OW9 and W17d) GAC pretreated	R	8.9	6.0-11.9	542	98	57-163	21	82	59-100	Effluent from GAC Study 9 used for GAC Study 12

(Continued)

TABLE 20. (Continued)

		OPERATING CONDITIONS							REMOVAL		
STUDY NO.	WASTEWATER	REACTOR TYPE	HRT (hr)		TOC LOADING			No. of Data Points	TOC REMOVAL		COMMENTS
			AVER	RANGE	mg/l AVER	Lb/1000cu.ft./day AVER	RANGE		AVER	RANGE	
31	composite (OW9 and W17d) GAC pretreated	R	7.9	7.3-9.8	762	139	110-202	24	76	49-98	Effluent from GAC Study 10
32	composite (OW9 and W17d)	R	17.2	13.9-20.8		57	51-72	8	68	63-83	PAC added to aeration chamber
33	composite (OW9 and W17d) ozone pretreated	S	21.7	16.2-29.2	519	37	14-77	22	47	32-66	
34	composite (OW9 and W17d) ozone pretreated	S	5.7	4.9-7.1	777	206	102-304	35	48	30-61	
35	composite (OW9 and W17d) ozone and GAC pretreated	S	6.5	5.8-7.5	540	131	65-209	23	50	21-78	Effluent from GAC Study 11
36	composite (OW9 and W17d) ozone pretreated	S	5.5	4.9-5.8	861	243	209-266	5	44	30-54	Activated sludge effluent
37	composite (OW9 and W17d) GAC and UAF pretreated	R	9.7	8.3-12.8	96	15	3-31	17	37	0-79	Effluent from GAC Study 16
38	composite (OW9 and W17d) GAC and UAF pretreated	R	9.8	7.2-12.8	69	11	2-36	10	40	0-100	Effluent from GAC Study 17
39	OW9 groundwater	S	6.3	5.6-7.5	1347	317	244-410	13	30	15-52	
40	OW9 groundwater	S	12.1	10.8-13.9	1907	236	193-299	15	50	10-67	
41	OW9 groundwater	S	13.1	11.2-15.4	1992	215	179-279	9	56	35-65	
42	OW9 groundwater GAC pretreated	R	10.4	9.3-11.6	1263	182	75-300	11	72	34-82	Effluent from GAC Study 14
43	OW9 groundwater GAC pretreated	R	10.4	8.8-11.9	1323	191	151-237	7	55	32-81	Effluent from GAC Study 15
44	W17d groundwater	S	5.9	5.8-6.6	181	47	32-64	13	53	38-72	
45	W17d groundwater	S	10.4	9.7-11.2	222	32	26-40	15	53	23-75	
46	W17d groundwater	S	14.1	12.1-17.1	228	25	16-34	5	42	22-57	

R - 1 liter reactor unit
S - 350 ml Swisher unit
GAC - Granular Activated Carbon
UAF - Upflow Anaerobic Filter
PAC - Powdered Activated Carbon

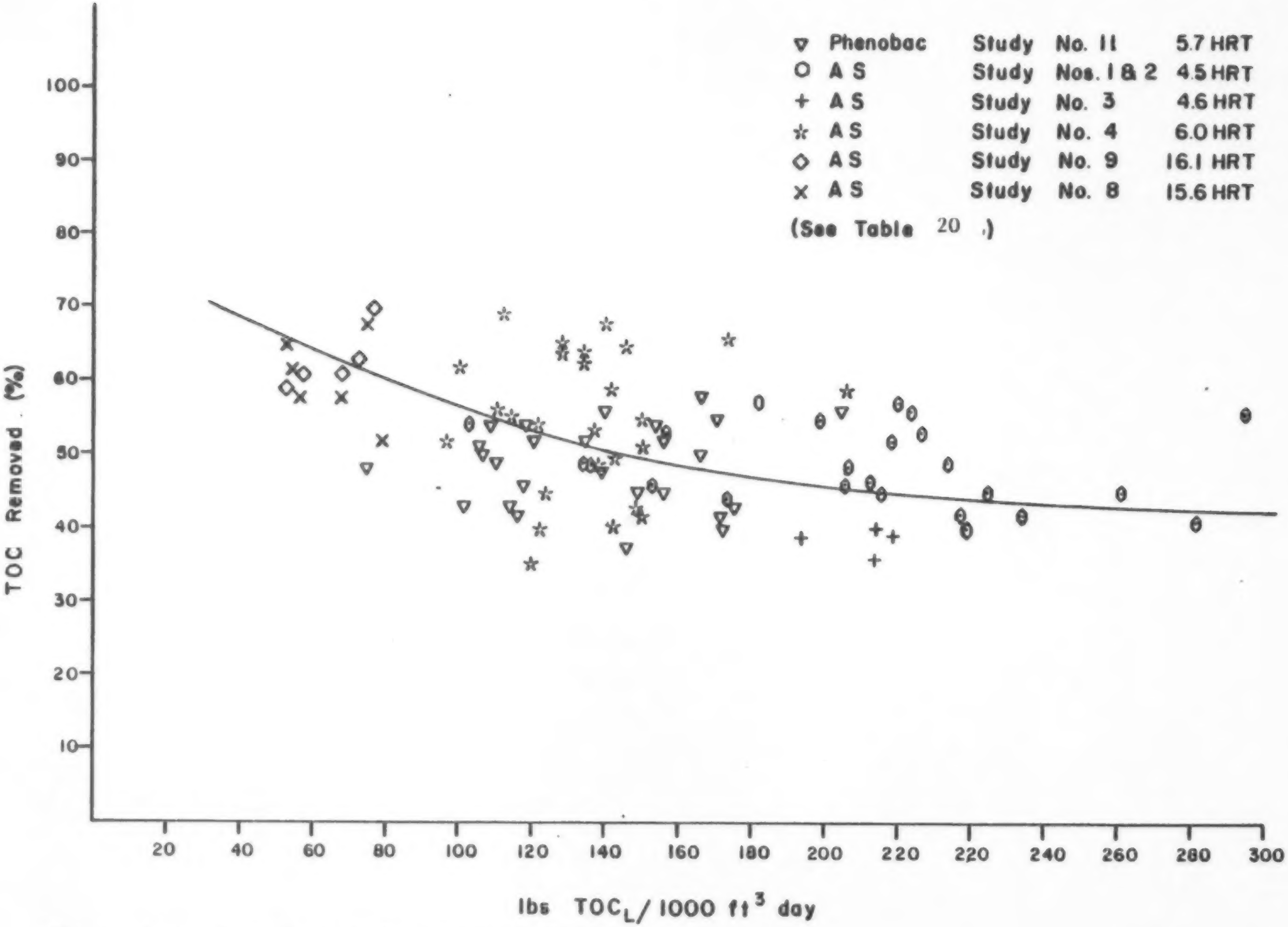


Figure 23. Activated Sludge TOC Removals.

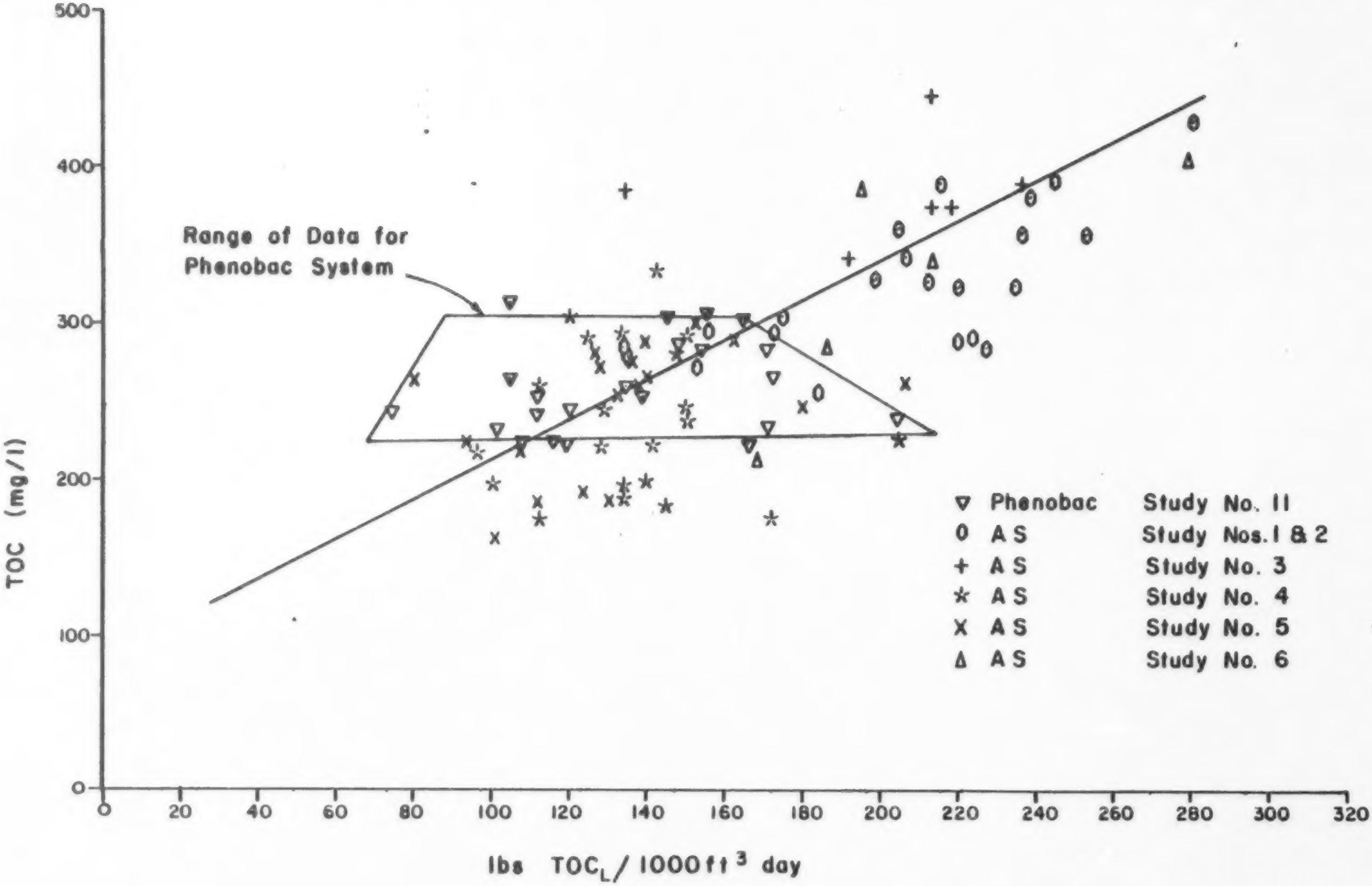


Figure 24. Activated Sludge Effluent TOC Concentrations.

A commercially available bacterial culture adapted for hydrocarbon degradation also was studied. Phenobac® provided by Polybac Corporation was selected because of its reported suitability for the type of wastewater occurring at the Ott/Story site. The culture was prepared according to Polybac's instructions. Both the Phenobac® system and the conventional activated sludge system were fed only raw groundwater. Operating conditions are shown in Table 20. The Phenobac® system achieved an average TOC reduction of about 48 percent with a range of 37-58 percent. There was no observed advantage to the use of Phenobac® based on effluent TOC.

Adsorption Pretreatment/Biological Treatment Process Trains

Adsorption/Activated Sludge System --

As a result of marginal performance by both conventional activated sludge and Phenobac® systems using raw groundwater, additional activated sludge studies were conducted using groundwater pretreated by (a) sorption using granular activated carbon (GAC), (b) organic resin, (c) chemical oxidation via ozone, (d) GAC and ozone, (e) GAC and upflow anaerobic filter processing and (f) the addition of powdered activated carbon (PAC) to the aeration chamber.

Studies 12 through 22 and 27 through 31 summarized in Table 20, were conducted to study the influence of GAC pretreatment on activated sludge performance. Although a variety of operating conditions were investigated, results were found to be fairly consistent. Figure 25 illustrates performance of the activated sludge process in the GAC/activated sludge process train during studies 15 through 22 and 31. Figure 26 summarizes daily results; these data are judged to be representative of all studies. To normalize variations in wastewater composition from run to run, influent loading to the GAC/activated sludge process train is presented on the basis of cumulative TOC loading per unit weight of activated carbon.

It was found that GAC pretreatment of raw groundwater permitted development of a culture of aerobic organisms capable of further treating GAC effluent. In excess of 95 percent TOC removal was achieved by this process train during the period when the GAC process accounted for at least 30 percent of the TOC removal. After this initial period, process train performance declined as GAC performance declined. These data indicate that some fraction of TOC began to leak through the system after a short period of operation. The fraction of TOC which leaked through the GAC system was not toxic to activated sludge (AS). These organics did not appear to be removed or reduced either biologically or by the air stripping associated with AS aeration.

Operation of the AS portion of this process train at hydraulic retention times (HRTs) ranging from 4 to 16 hr, with or without the addition of powdered activated carbon to the biological reactor, or with or without Phenobac® addition seemed to have little impact on process train performance (based upon TOC removal). Overall system performance was maintained at 75 to 85 percent TOC removal (effluent TOC of 100 to 185 mg/l) for about 21 days. This represents processing of more than 110 BVs for the GAC process and 46 retention times for the AS process. Results of these studies are illustrated in Figure 27. Although not illustrated in the figure, Phenobac® subsequently was added

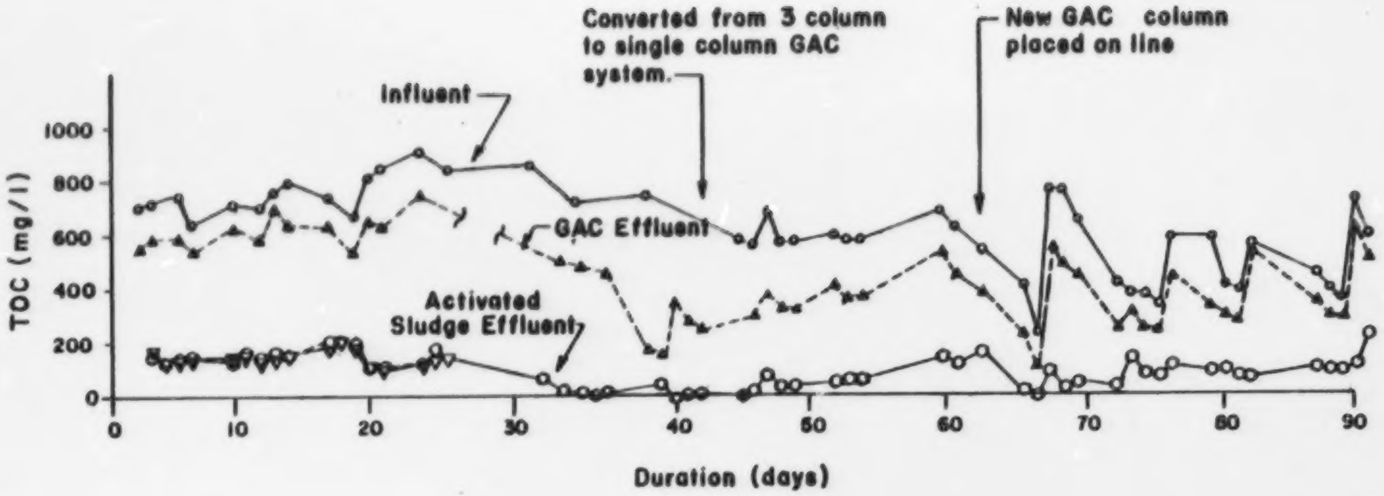


Figure 25. Performance of GAC/Activated Sludge Process Train.

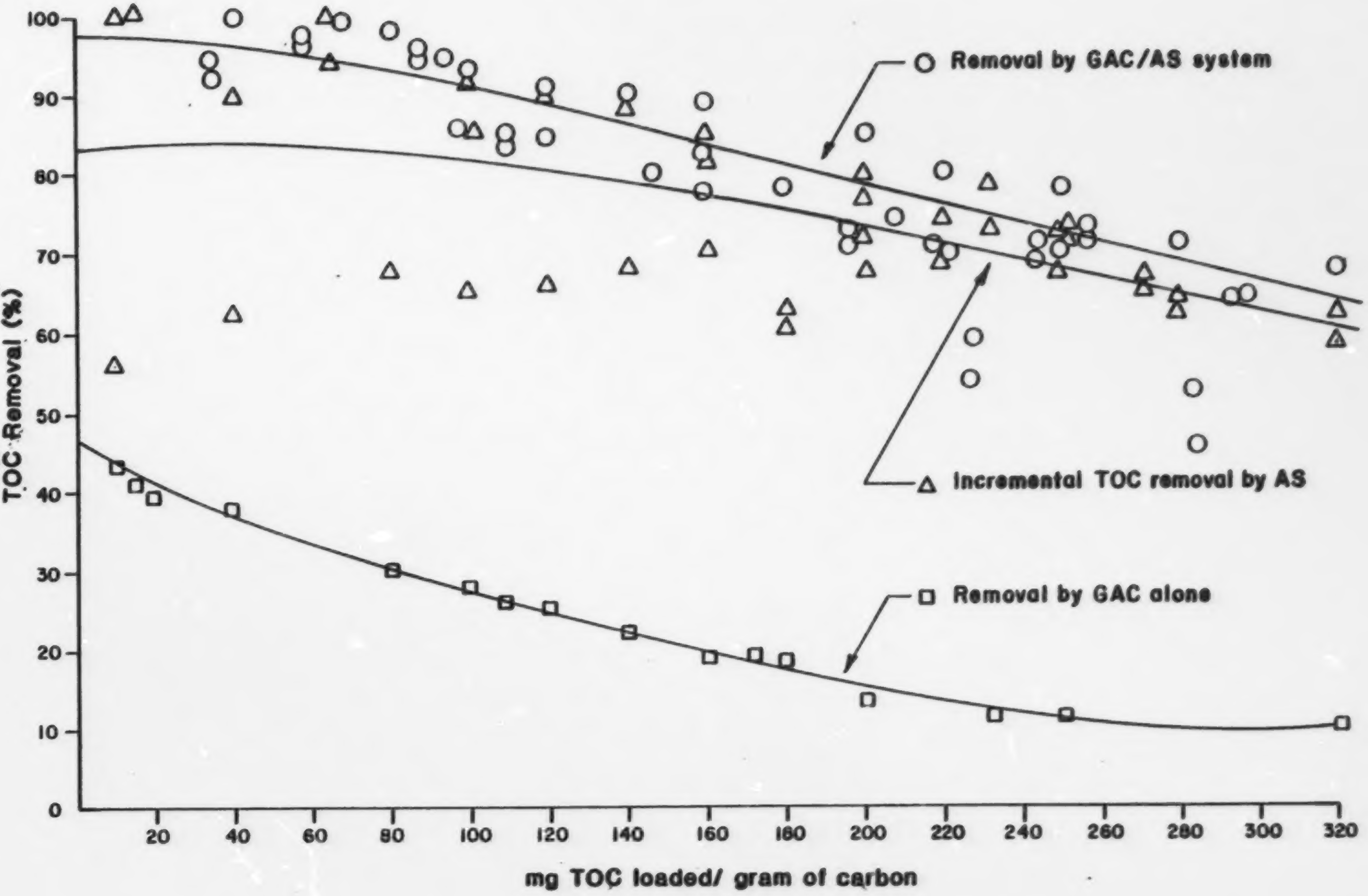


Figure 26. TOC Removal by GAC/Activated Sludge Process Train.

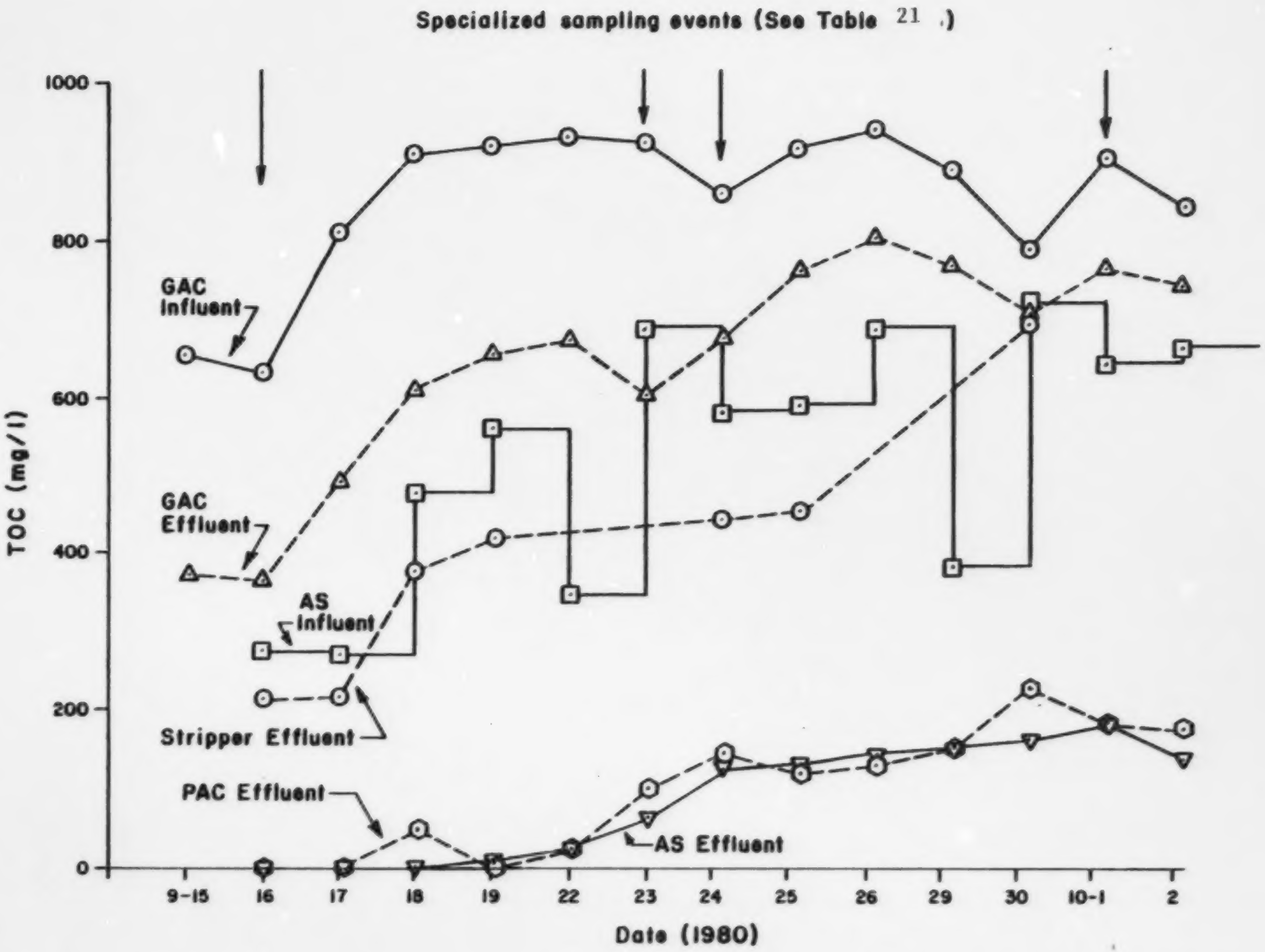


Figure 27. Performance of GAC and Activated Sludge Process Modifications.

to one of the reactors during the course of this run. There was no difference in TOC removal between the Phenobac® reactor (operated at 6 hr HRT) and the conventional AS reactor (operated at 16 hr and 6 hr HRTs). As TOC leakage from the GAC process increased, biological process removal performance diminished. Conventional AS and Phenobac® reactor effluents contained about 200 mg/l TOC when this phase of the study was completed. Visual observations and typical mixed liquor analyses (MLSS and MLVSS) suggest that the biological systems could survive in and utilize GAC pretreated groundwater even after GAC performance had declined to about 10 percent TOC removal.

During the entire two month duration of this phase of study, TOC removal by the GAC/AS process train varied from 100 to 74 percent. Effluent TOC could be maintained at levels less than 100 mg/l only for short periods of time and only when GAC performance was at its peak. Limited analyses, however, suggest that high levels of organic priority pollutant removals can be attained even with effluent TOC concentrations of 100 to 200 mg/l. Table 21 presents results of GC/MS analyses for organic priority pollutants conducted at several times during the operation of the GAC/AS process train. Almost all organic priority pollutants detected in raw groundwater were removed consistently to less than the level of detection (0.01 mg/l) by the process train. One consistent feature of these data and previous GC/MS analyses from batch carbon adsorption studies is the early leakage of 1, 2-dichloroethane. A few other compounds (benzene, methylene chloride, and toulene) also were detected to have broken through in some batch and continuous flow studies. The acid and base neutral extractable compounds generally did not break through the GAC process.

Data in Table 21 indicate that the activated sludge process completely removed the few organic priority pollutants leaking through the GAC system even though overall TOC removal declined. The continued removal of organic priority pollutants may be due to stripping, biological degradation, or adsorption to sludge floc.

As expected, neither the GAC nor AS process effected removal of either total cyanide or CN_A. However, greater than 99 percent total phenol removal was observed, which is consistent with results of previous studies.

An off-gas sample from the aeration chamber of the activated sludge reactor was collected using a cold trap (acteone and dry ice) to condense and freeze off-gas vapors. Air flow to the reactor was approximately 2 l/m and the collection period was four hours. The following organic priority pollutants were detected in this sample:

Methylene Chloride	1.02 μg/l air
1,2-Dichloroethane	1.04 μg/l air
Benzene	0.250 μg/l air
Perchloroethylene (tetrachloroethylene)	0.125 μg/l air
Toluene	0.0875 μg/l air

TABLE 21. TOC AND SPECIFIC POLLUTANT DATA FOR GRANULAR ACTIVATED CARBON/ACTIVATED SLUDGE PROCESS TRAIN (mg/l)

[Dates of Sampling shown on Figure 27]

Compound	Raw Ground-water 9-16	GAC Effl. 9-16	Raw Ground-water 9-23	GAC Effl. 9-23	AS Effl. 9-24	GAC Effl. 10-1	AS Effl. 10-1
TOC	637	380	929	604	90	770	183
Total Cyanide	NA	NA	0.11	0.21	0.23	0.23	0.20
CN_A	NA	NA	<0.05	<0.05	<0.05	<0.05	<0.05
Total Phenol	NA	NA	16	<0.16	<0.10	<0.10	<0.10
Methylene chloride	2.1	0.029	14	0.01	ND	0.16	ND
1,1-Dichloroethene	1.6	ND	0.06	0.01	ND	ND	ND
1,1-Dichloroethane	2.4	ND	0.17	0.02	ND	ND	ND
Trans-1,2-dichloroethane	0.06	ND	0.04	ND	ND	ND	ND
Chloroform	9.8	ND	0.70	0.06	ND	ND	ND
1,2-Dichloroethane	72	ND	25	1.4	ND	0.05	ND
1,1,1-Trichloroethane	7.6	ND	0.39	0.04	ND	ND	ND
Trichloroethylene	0.06	ND	0.03	ND	ND	ND	ND
Benzene	1.2	ND	1.5	0.02	ND	ND	ND
1,1,2-Trichloroethane	0.11	ND	0.07	ND	ND	ND	ND
Perchloroethylene	0.49	ND	1.9	ND	ND	ND	ND
Toluene	2.3	ND	0.97	0.05	ND	0.01	ND
Chlorobenzene	0.23	ND	0.029	ND	ND	ND	ND
Phenol	0.025	ND	0.028	ND	ND	ND	ND
2-Chlorophenol	0.040	ND	0.036	ND	ND	ND	ND
2,4-Dichlorophenol	0.010	ND	0.010	ND	ND	ND	ND
1,2-Dichlorobenzene	0.085	ND	0.077	ND	ND	ND	ND
Dibutyl phthalate	ND	ND	ND	ND	0.05	ND	ND

NA - Not Analyzed
ND - Not Detected
No other priority pollutants detected at 0.01 mg/l detection limit

XE-347 resin also was examined as a pretreatment adsorption process. Operating conditions for resin adsorption were as follows:

- 3 columns in series
- columns were 2.54 cm diameter and contained resin bed depths of 48.3 cm, 55.9 cm, and 52.1 cm, respectively
- total BV = 792 cm^3
- downflow operation at 41 to 50 ml/min (3.11 to 3.79 BV/hr)
- EBCT ranged from 19 to 16 min

When the pretreatment process was converted from GAC to XE-347, there was a rapid loss in TOC removal capacity. A second resin trial produced similar results. In both cases, TOC removal diminished to less than 59 percent after about five bed volumes were loaded and appeared to stabilize at 10-20 percent removal for at least 120 BV. The shape characteristics of the TOC breakthrough curves are similar to those of GAC except that TOC removal declined much more rapidly. The period of operation with XE-347 resin was from day 2 through day 27 in Figure 25. Subsequently the adsorber was switched to activated crabon whereupon overall performance improved substantially. As shown on Table 22, activated sludge units following resin pretreatment were not able to produce effluents containing less than 100 mg/l TOC.

Adsorption/Anaerobic Biological System--

Anaerobic biological treatment was believed to be a candidate treatment process because of the high organic content of the groundwater and because the air pollution potential associated with volatile priority pollutant stripping in the activated sludge process could be avoided.

Operating conditions for the upflow anaerobic filter (UAF) apparatus, which is described in Section 3, were as follows:

- organic loading rate 26.4 to 52.9 lb TOC/1000 ft^3/d
- hydraulic flow rate ~ 1.15 to 2.0 ml/min
- EBCT ~ 13.1 to 22.8 hr
- temperature ~ 35°C

Performance of the GAC/UAF process train is illustrated in Figure 28. TOC removals by the process train and individual processes are summarized below:

	average	range
TOC removal by GAC/UAF train:	66%	38-81%
TOC removal by GAC process:	31%	10-46%
TOC removal by UAF process:	50%	12-67%

TABLE 22. TOC REMOVAL BY XE-347 RESIN

Wastewater Processed (L)	Column 1		Column 2		Column 3	
	BV Loaded	% TOC Removal	BV Loaded	% TOC Removal	BV Loaded	% TOC Removal
3	12.2	20	5.68	38.5	3.79	57.0
6	24.5	16.3	11.4	23.7	7.58	23.0
12	50	9.6	22.7	18.5	15.2	20.0
17.5	71.4	25.2	33.1	35.6	22.1	39.9
24.9	102	10.4	47.2	17.8	31.4	19.0
29.8	122	10.4	56.4	16.0	37.6	19.0
Columns recharged with virgin resin						
2.46	8.57	31.9	4.49	43.9	2.95	66.7
4.92	17.1	19.9	8.98	29.8	5.89	33.9
9.92	34.3	18.7	18.0	24.6	11.8	33.9
14.8	51.6	15.8	27.0	21.1	17.7	25.7
17.2	59.9	10.9	31.4	18.6	20.6	23.0
22.1	77.0	8.2	40.3	16.9	26.5	16.9
27.0	94.3	8.2	51.1	14.8	32.3	18.0

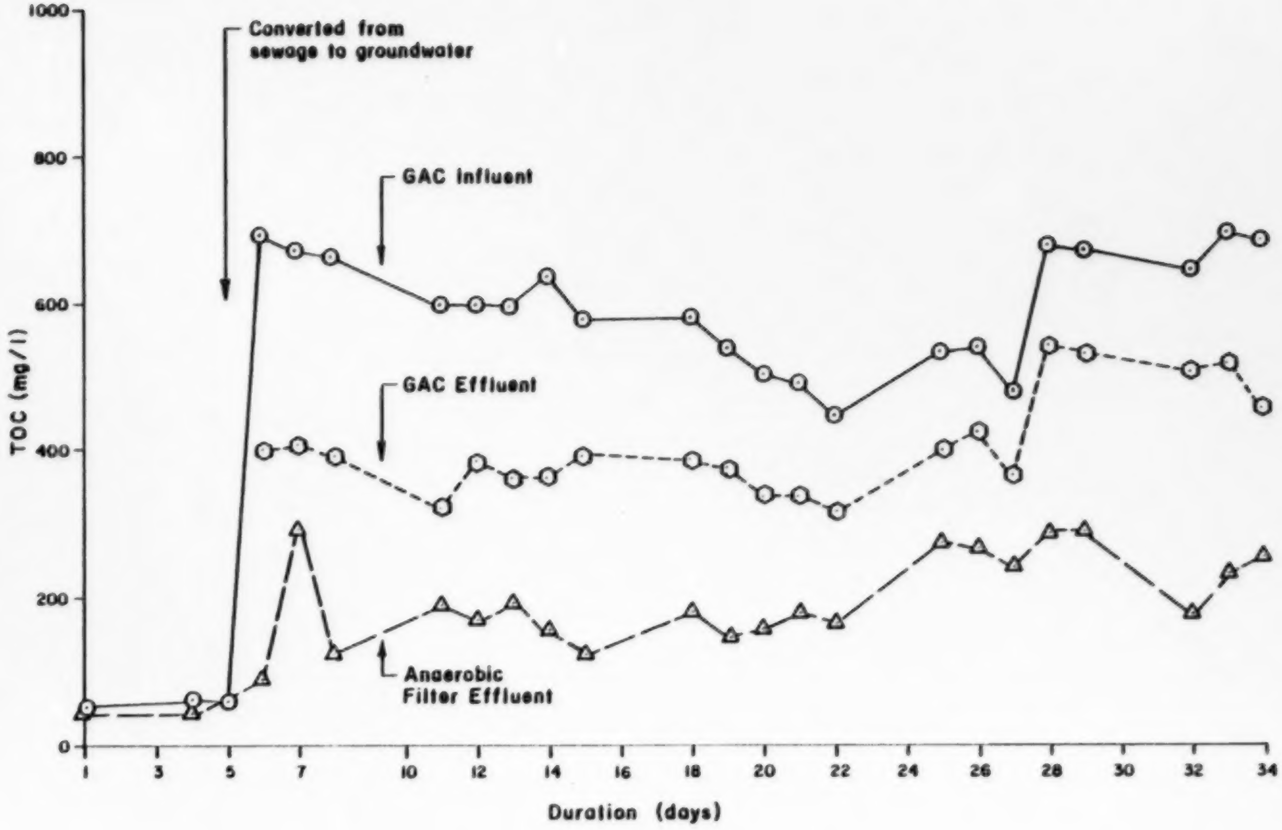


Figure 28. Performance of GAC/Anaerobic Filter Process Train.

UAF effluent TOC increased as TOC leakage from the GAC pretreatment process increased. Results of one six hour batch air stripping study indicated that UAF effluent contained about 40 percent (117 mg/l) strippable TOC at the time the sample was collected. Overall, the GAC/UAF process train, with an upper TOC removal limit of about 81 percent did not perform as well as the GAC/AS system.

Selected operational data (TOC loading, effluent pH, sludge pH, sludge total alkalinity, volatile acids concentration, and gas production) are indicated in Figure 29. Gas production during the study averaged 505 ml/g TOC fed. In an attempt to bring sludge pH into a range reported to be most optimal (pH 7.2 to 7.6), the GAC influent pH was adjusted to pH 7.0 to 7.5. This had no apparent effect on performance.

Figure 30 illustrates performance of a process train consisting of GAC/upflow anaerobic filter/activated sludge. These results indicated that performance of the AS process in the train is inversely proportional to GAC performance; that is, as leakage from the GAC column increased, the amount of overall removal attributable to the AS process increased. Data indicate that this largely may be due to stripping in the aerobic system. Batch air stripping tests showed minimal TOC removal from the UAF effluent when the GAC system was performing at its highest levels, whereas, 40 percent TOC removal by stripping was reported when GAC performance was poor. Performance of the entire system was not as good as the GAC/AS process train; i.e., it did not maintain low effluent TOC levels (less than 50 mg/l) for as long as the GAC/AS train. However, both systems appear to be able to produce effluent TOC levels below 100 mg/l for equivalent durations.

Chemical Oxidation Pretreatment with Ozone

Preliminary batch groundwater ozonation studies were conducted under the following conditions using a Welsbach Model T-408 laboratory scale ozone generator:

- ozone production using air feed
- ozone gas flow rate - 2 l/min
- ozone dose - approximately 2 g/hr (generator operating at 90V)
- contact time - up to 9 hr
- batch volume - 15 l

After conducting studies with distilled water to assure good mixing, ozone transfer studies using groundwater were completed. Ozone measurements were made according to Standard Methods (4) using the Iodometric Method.

After several preliminary batch ozonation studies which indicated little reduction in groundwater TOC (which would be expected in view of the parameter

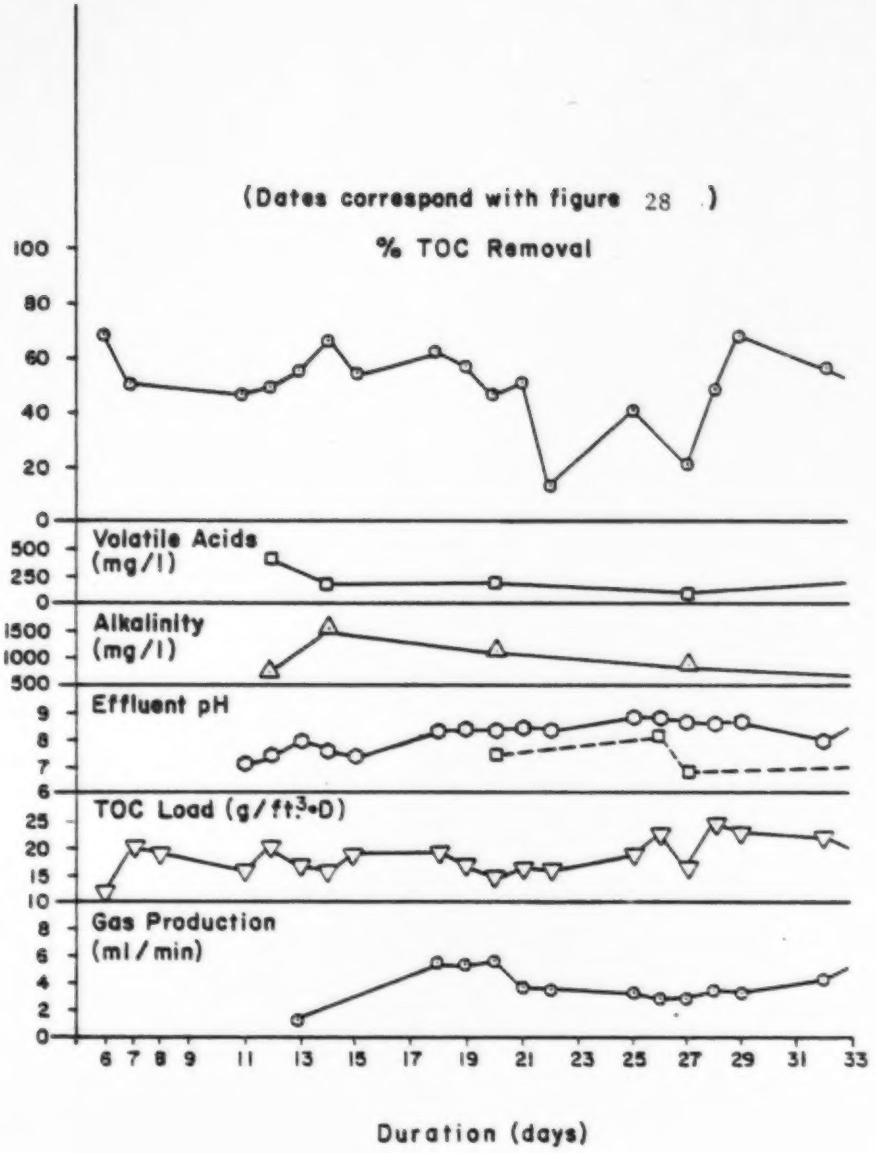


Figure 29. Anaerobic Filter Operation.

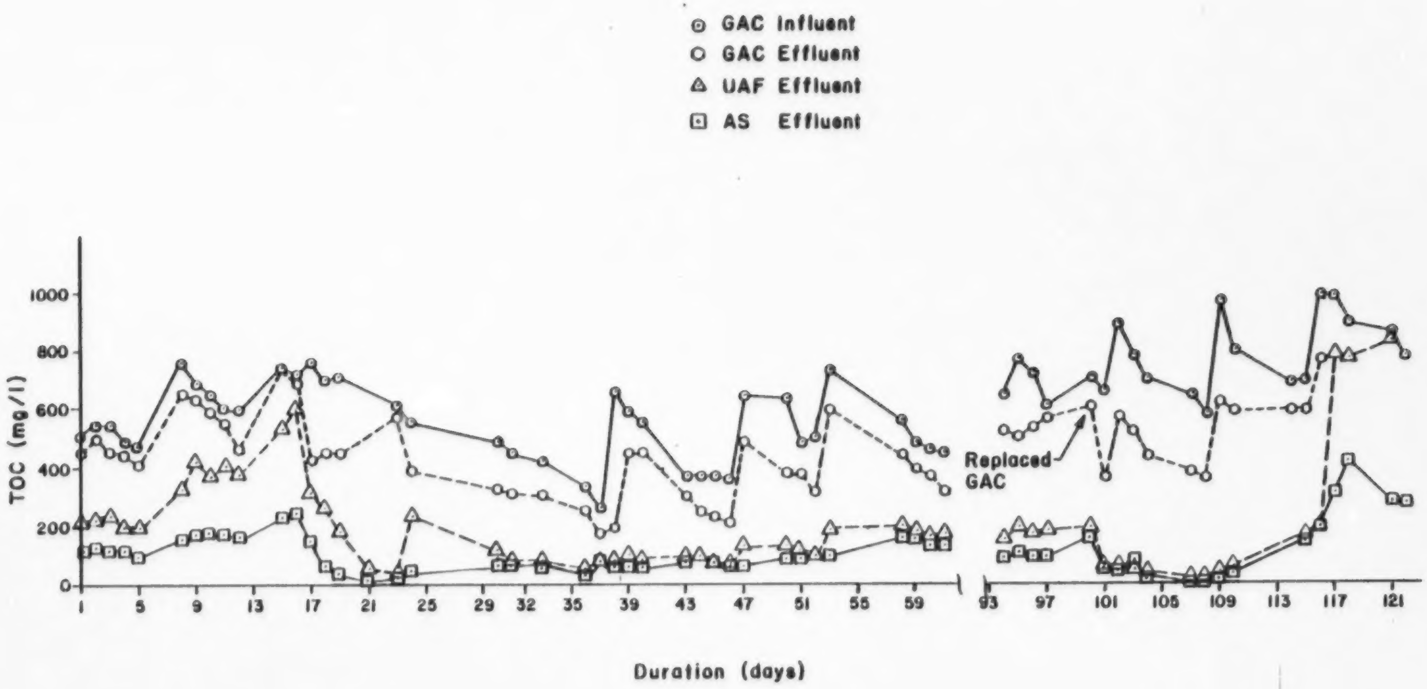


Figure 30. Performance of GAC/Anaerobic Filter/Activated Sludge Process Train.

being measured and the mechanisms of the ozone reaction), studies were made to determine if ozonation enhanced either adsorption or biological treatment.

Effects on adsorption were determined by ozonating a batch of raw groundwater and then conducting adsorption isotherm tests using activated carbon (FS-300) and resins (XAD-4, XE-340, and XE-347). To measure the effect of stripping during ozonation, a parallel system was operated at the same gas flow rate feeding air rather than ozone and adsorption isotherms were prepared. Operating conditions for these studies were as follows:

- air or ozone gas flows - 2 l/min
- air or ozone contact times - 2.5 hr
- groundwater batch volume - 7.5 l
- ozone dose - about 2 g/hr (at 90V)
- sorbent doses - 0.5 to 106 g/l
- sorbent contact time - 2 hr
- sample temperature - 22 to 25°C
- sample pH - 9.6

Results are summarized in Table 23. No clear difference in adsorption process performance was observed with the two pretreatment techniques (aeration and ozonation). As before, results did indicate better TOC removal by activated carbon than by resins.

Ozonation as a pretreatment before biological processes also was examined. Batch ozonated groundwater served as feed for an activated sludge process, and as feed for a GAC/AS process train.

Figure 31 illustrates results for a representative portion of these studies. They indicate that:

- preozonation did not improve AS performance which remained at about 40 to 50 percent TOC removal.
- preozonation did not improve performance nor extend TOC breakthrough characteristics of the GAC process.

Post-Treatment with Granular Activated Carbon

To provide a preliminary assessment of GAC as a polishing rather than a pretreatment process, an isotherm study was conducted with effluent from the O_3/AS train using FS-300 powered activated carbon. Then, a continuous flow GAC column was placed on-line to form a O_3/AS/GAC process train. Results of the isotherm study, conducted with O_3/AS effluent (282 mg/l TOC) after two hours contact time are presented below:

TABLE 23. SUMMARY OF BATCH OZONATION AND ADSORPTION STUDIES

SAMPLE	SORBENT	SORBENT DOSE (g/l)	FINAL TOC C_f (mg/l)	TOC SORBED X(mg/l)	SORBENT LOADING X/M(mg/g)	OVERALL TOC REMOVAL(%)
Raw groundwater	-	-	1050	-	-	-
Blank-groundwater after ozonation		-	1020	-	-	-
Blank-groundwater after aeration		-	1020	-	-	-
Blank-ozonation and shaking		-	985	-	-	-
Blank-aeration and shaking		-	940	-	-	-
Ozonated	FS 300	0.5	900	85	170	14.3
		5	815	170	34	22.4
		50	633	352	7.0	39.7
		106	573	412	3.9	45.4
	XAD 4	0.5	984	1	2	6.3
		5	942	43	8.6	10.3
		50	882	103	2.1	16.0
		106	852	133	1.2	18.9
	XE-340	0.5	970	15	30	7.6
		5	950	35	7	9.5
		50	920	65	1.3	12.4
		106	888	97	0.9	15.4
	XE-347	0.5	985	0	0	6.2
		5	930	55	11	11.4
		50	830	155	3.1	21.0
		106	730	255	2.4	30.5
Aerated	FS 300	0.5	876	64	128	16.6
		5	754	186	37.2	28.2
		50	609	331	6.6	42.0
		106	560	380	3.6	46.7
	XAD 4	0.5	925	15	30	11.9
		5	912	28	5.6	13.1
		50	850	90	1.8	19.0
		106	767	173	1.6	27.0

a. Calculated on the basis of raw groundwater TOC and final TOC after adsorption

Sorbent contact time - 2 hr

Sample pH - 9.6

Sample temperature - 22 to 25°C

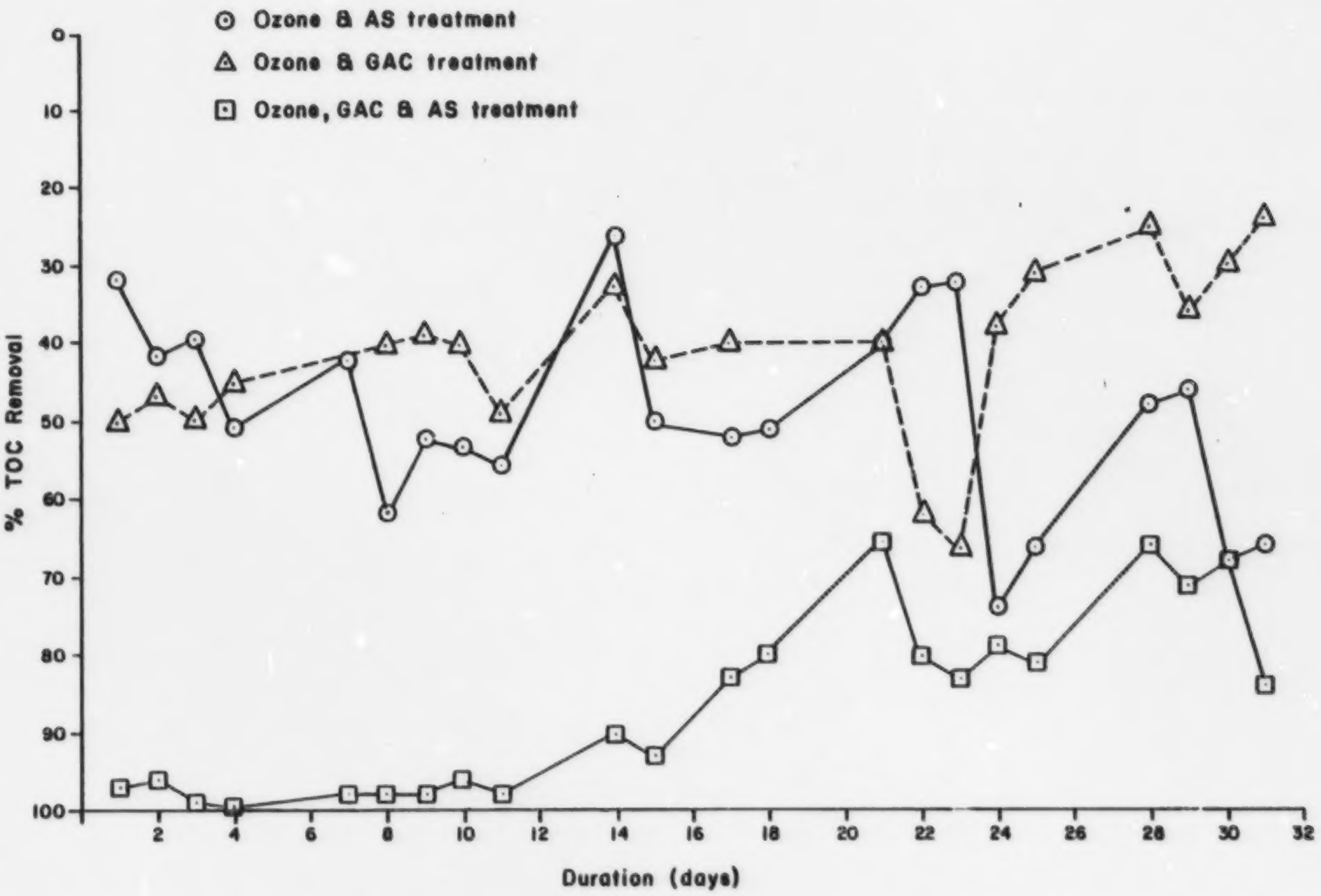


Figure 31. Comparison Between Process Trains Using Ozone.

M carbon dose	C_f final TOC (mg/l)	X/M TOC adsorbed (mg/g carbon)
0	274	-
0.5 g/l	233	82
5. g/l	144	26
50. g/l	20	5.1
100. g/l	6	2.7

These data are illustrated by the isotherm shown in Figure 32. Comparing some of these data with previously presented sorption isotherm data for raw groundwater and ozone pretreated groundwater suggests that much lower effluent TOC concentrations can be produced by the process train of O_3/AS/GAC. However, continuous flow operation of the O_3/AS/GAC process train showed no advantage to GAC polishing. Under the following operating conditions for the GAC process, the O_3/AS/GAC process train was less efficient than the GAC/AS train:

hydraulic loading rate: 0.5 gpm/ft^2

EBCT: 2.3 hr

72 BVs processed (~65.9 mg TOC loaded/g GAC)

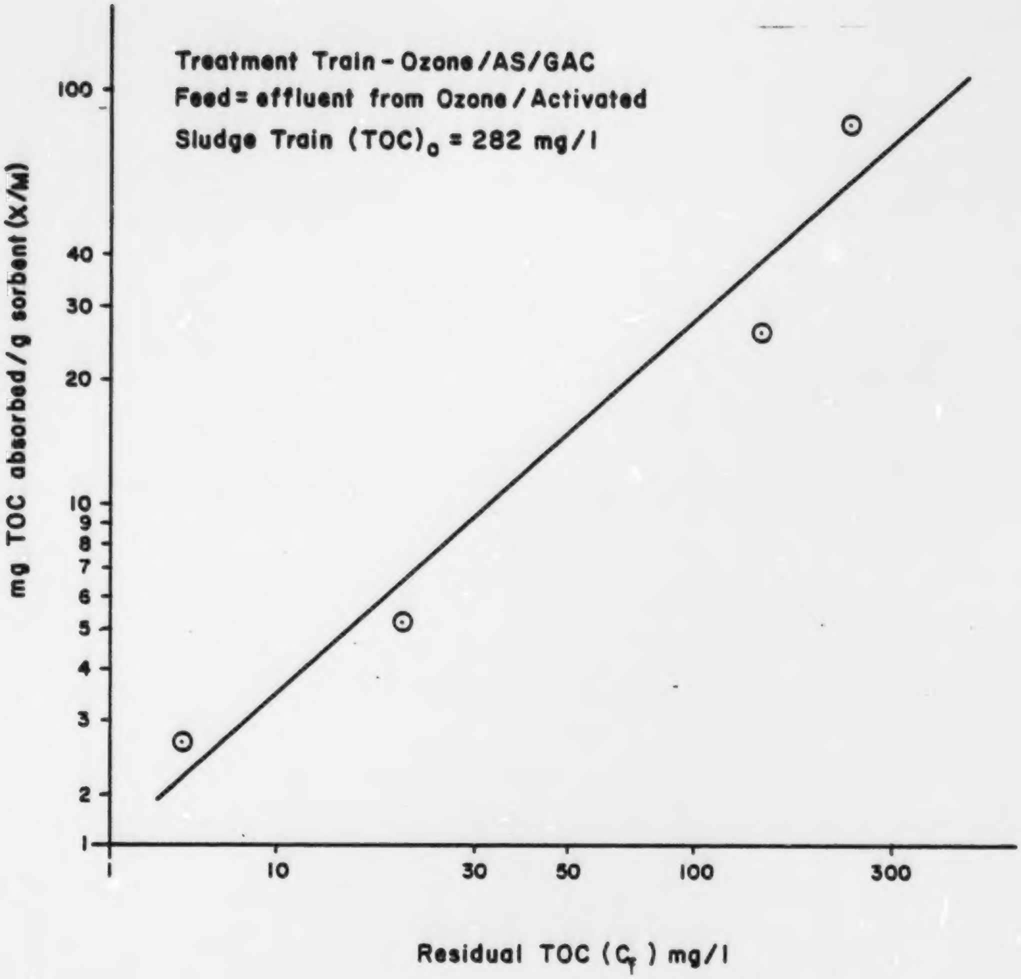


Figure 32. Adsorption Isotherm, Composite Groundwater Pretreated by Ozone/Activated Sludge.

SECTION 5

STUDIES USING GROUNDWATER FROM THE GRATIOT COUNTY LANDFILL

BACKGROUND

The Gratiot County Landfill located near St. Louis, Michigan was used primarily for disposal of municipal solid waste; however, between 1971 and 1973 122,000 kg (269,000 pounds) of waste containing 60% to 70% polybrominated/biphenyls (PBB) also was disposed there (6). As a result of a previous PBB incident in Michigan in 1977, the Department of Natural Resources (MDNR) began investigating site conditions. PBB and other contaminants were found in the shallow groundwater aquifer; isoconcentration contour maps were prepared for several parameters. Table 24 summarizes groundwater quality in the middle sand aquifer.

Because one remedial measure under consideration at Gratiot County Landfill involved encapsulation by installation of an impermeable cover and subsurface barrier and a well point system for groundwater withdrawal, MDNR expressed interest in the on-going Baker/TSA groundwater treatability project. Groundwater quality at Gratiot County Landfill differed considerably from that at the Ott/Story site; thus it was believed that this waste stream would provide a different set of conditions to evaluate selected technologies. The technologies judged to be suitable candidates were granular activated carbon adsorption, coagulation/precipitation, sedimentation, filtration, ion exchange, and reverse osmosis.

PROCEDURES

Of the numerous existing monitoring wells, well DW-7 was selected for use in this study because previously it had yielded among the more highly contaminated samples and also because the volume yield was sufficient to collect the quantities of groundwater necessary for experimental studies. Samples from well DW-7 were collected by MDNR personnel. The procedure involved evacuating five well volumes using a manual bailer, allowing the well to recharge, and then sampling. Samples were placed in 18.9 l (five gallon) polyethylene carboys, and shipped to Baker/TSA's laboratory in Beaver, Pennsylvania. The time span between sample collection and receipt at the laboratory was about 24 hours. No preservatives were added at the time of collection or receipt. Instead, one carboy from the sampling batch was selected for immediate use and others were frozen until needed. As required, carboys were allowed to thaw at room temperature prior to use. Freezing was judged to be the most suitable preservation method to minimize transformations which would affect technology evaluations without detrimentally affecting waste stream properties. Prior to

TABLE 24. GRATIOT COUNTY LANDFILL QUALITY OF MIDDLE SAND AQUIFER(1)

PARAMETER	CONCENTRATION RANGE (mg/1)
PBB	0.012 - 0.12 μg/1
Chemical Oxygen Demand	1.0 - 140
Total Dissolved Solids	290 - 710
Total Organic Carbon	0.90 - 24.0
pH	7.1 - 11.6
Ammonia Nitrogen	0.02 - 0.59
Total Kjeldahl Nitrogen	0.02 - 13.0
Chloride	1.0 - 89.0
Sulfide	0.01 - 1.2
Hardness	36.0 - 760.0
Chromium	0.004 - 0.40
Iron	0.91 - 80.0
Nickle	0.010 - 0.11
Lead	0.001 - 0.58
Zinc	0.2 - 87.0
Cadmium	0.002 - 0.049
Phenol	0.003 - 0.28
Bromine	0.002 - 1.9
Arsenic	0.003 - 0.038

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(1) Source: Michigan Department of Natural Resources. Hydrogeological Investigation and Engineering Alternatives for Control Measures Gratiot County Landfill Michigan. Resource Recovery Division, Department of Natural Resources, Lansing, Michigan. June, 1979.

freezing, a representative sample was withdrawn and analyzed for PBB, and total and dissolved metals including most priority pollutant metals. Results were compared with drinking water standards and other water quality criteria to identify areas of concern and principal parameters to measure treatment process effectiveness. Initial technology evaluations then were designed.

Granular media filtration was evaluated on a batch basis using a 50 ml buret containing 23 ml of white sand which passed a No. 40 sieve (~0.0165 inch particle size). Flow rate was 9.5 ml/min. (approximate surface loading rate of 1.8 gpm/ft.^{2}). Sample collection spanned the period between the passage of 74 through 99 bed volumes.

Gravity sedimentation was examined on a batch basis by monitoring quiescent settling in a one liter beaker. Turbidity initially was used to measure performance. Results indicated that turbidity decreased from 150 NTU to 100 NTU in 15 minutes and stabilized at about 85 NTU after 1 to 3 hours. Subsequently supernatant samples were drawn after 1 hour for analysis of the metals of concern.

Following batch evaluation of granular media filtration and gravity sedimentation, the following continuous flow studies where initiated:

- sand filtration using a 2.54 cm ID by 32.5 cm Plexiglas column
- granular activated carbon (GAC) using a 1.9 cm ID by 133 cm Plexiglas column
- sand filtration followed by GAC using columns similar to those described above

Once these studies had begun, raw groundwater being used was found to have low metal concentrations and no PBB at a detection level of 0.001 mg/l (although 0.68 mg/kg of PBB was measured in sediment filtered from the groundwater samples). Therefore, in view of the raw groundwater quality, continuous flow evaluations were discontinued.

RESULTS

Analysis of samples initially received at the Baker/TSA laboratory indicated that metals were predominantly in the insoluble form. Thus, batch evaluation of granular media filtration and gravity sedimentation were examined first. Results along with raw groundwater quality data are summarized in Table 25. Only the metals found to exceed interim primary drinking water standards or water quality criteria were used to monitor process performance. Granular media filtration and gravity sedimentation (without pH adjustment or chemical additives) provided significant removal of the insoluble fraction of the metals.

It was concluded that these physical separation processes effectively remove metals associated with silt in the sample. Because PBB also appears to be associated with the silt, it is expected that these processes also would achieve significant levels of PBB removal.

TABLE 25. GRATIOT COUNTY LANDFILL GROUNDWATER METALS CONTENT - RAW AND TREATED

Parameter	Raw Groundwater Total[a] (mg/1)	Raw Groundwater Soluble[b] (mg/1)	Typical Well DW-7[c] (mg/1)	Sand Filtration Effluent (mg/1)	Gravity Sedimentation Supernatant Total[a] (mg/1)	Gravity Sedimentation Supernatant Soluble[b] (mg/1)
Arsenic	<0.02	<0.02				
Beryllium	<0.002	<0.002				
Cadmium	0.02	0.01	<0.003	0.01	0.02	<0.01
Chromium	0.05	<0.02	0.024	0.07	<0.02	
Copper	0.20	0.02				
Lead	0.11	<0.03	0.58	<0.03	<0.03	
Mercury	0.0001	<0.0005				
Nickel	0.10	0.06	0.011	0.04	0.04	
Selenium	0.055	0.008				
Silver	<0.01	<0.01				
Zinc	12.8	1.56	3.1	2.88	3.00	
Iron	31.6	<0.03	7.1	0.20	2.28	

a. Sample was digested for total metals

b. Sample was filtered and acidified before analysis

c. Hydrogeological Investigation and Engineering Alternatives for Control Measures Gratiot County Landfill, Michigan Resource Recovery Division, DNR, Lansing, MI. Final Report June, 1979 Exhibit 14, Parts J-O

SECTION 6

STUDIES USING LEACHATE FROM THE MARSHALL LANDFILL

BACKGROUND

Marshall Landfill located in Boulder County, Colorado is a privately operated, predominantly municipal solid waste landfill that accepted some industrial wastes from surrounding light manufacturing and fabricating industries. In 1979, seepage was observed to be draining from the fill into a small surface waterway used to convey water from Marshall Lake to the Louisville Reservoir which is part of the drinking water supply for Louisville, a nearby Boulder County municipality. Analysis of the seepage indicated the presence of numerous priority and non-priority organic compounds at concentrations varying from less than detection levels to about 6 mg/l. Table 26 summarizes available seepage and groundwater composition data at several sampling locations at the landfill.

PROCEDURES

Seepage collected in an impoundment designated as Lagoon 2 was selected for use in laboratory technology evaluations. Although limited composition data were available for this location, the TOC was significant (168 mg/l). Moreover, an adequate volume of sample for use in treatability studies could be collected easily and dependably which was not the case for other locations. Samples were collected by Boulder County Health Department personnel in five-gallon polyethylene carboys, express air shipped to the Baker/TSA laboratory and initially either used immediately or frozen. However, it was found that freezing altered sample composition. Samples frozen and then thawed at room temperature had TOC concentrations up to 58 percent lower than the concentration prior to freezing. As a result, it was necessary to store subsequently obtained samples in tightly closed, five-gallons shipping containers at room temperature until needed for use in the study.

The evaluation protocol using Marshall Landfill seepage is outlined below:

(1) Batch adsorption isotherm tests with 0.5 to 2.5 g/l doses of the following sorbents:

TABLE 26. ANALYSES OF WATERS AT MARSHALL LANDFILL

Contaminant	Concentration (mg/l)		
	Well 1	Leachate Seep	Lagoon 2
methylene chloride	2.00, 2.183	0.061, 0.200	
1,1-dichloroethane	0.100, 0.413	0.045, 0.100, 0.194	*
1,2-dichloroethylene	0.053	0.050, 0.130	
benzene	0.100		0.011
toluene	0.724, 1.200	<0.010, 0.020	
ethylbenzene	0.0100, 0.110	*	
1,1,1-trichloroethane	0.021	0.100, 0.227	
chlorobenzene	*		
vinyl chloride	0.182	<0.010, 0.014	
trichlorofluoromethane	0.112	<0.010, 0.078	
1,1,2,2-tetrachloroethane		*	
2-ethoxypropane		*	
trichloroethylene	0.300, 0.616	0.010, 0.040, 0.053	
chloroform	*	*	
chloroethane	*	<0.010, 0.018	*
1,2-transdichloroethylene	1.000, 5.65	<0.010, 0.202, 0.062	
1,2-dichloropropane	0.014		
methyl chloride	0.010		
dichlorodifluoromethane	0.292	0.065	
tetrachloroethylene	0.300, 0.616	0.035, 0.1000, 0.162	
1,3-dichloropropylene		*	
bis(2-ethylhexyl) phthalate		<0.010, 0.012	*
acenaphthene		*	
butylbenzyl phthalate		*	
di-n-butyl phthalate	0.033	*	*
diethyl phthalate	0.217	*	0.012
phenol	0.088	0.272	*
2,4-dimethylphenol			*
acrolein			*
TOC			168

*Detected at less than 10 µg/l

activated carbon: Calgon FS-300

Westvaco Nuchar SA

Darco HDC

resins: Rohm and Haas XAD-4 (polymeric)

Rohm and Haas XE-340 (carbonaceous)

Rohm and Haas XE-347 (carbonaceous)

(2) Aerobic biological treatment using the activated sludge process - A culture of activated sludge organisms was obtained from a large publicly owned treatment works having a substantial industrial contribution. This sludge was used to seed a Swisher reactor which then was fed Lagoon 2 wastewater at a rate that maintained a hydraulic retention time of 6 hours. Attempts to acclimate an activated sludge culture to raw seepage continued over a four-week period.

(3) Continuous flow adsorption tests - Continuous flow granular activated carbon (GAC) systems consisting of two or three columns in series were operated. Columns were 1.90 cm ID (0.75 in). The two-column system was loaded with approximately 167 g of FS-300 GAC; the three-column system contained about 268 g of FS-300 GAC. Additional system operation details are provided below.

(4) Activated sludge treatment of GAC pretreated seepage - A process train consisting of one 1.9 cm (0.75 in) ID GAC column containing about 87 g of FS-300 GAC followed by a one liter activated sludge reactor was used to determine if GAC pretreatment enhanced activated sludge performance in a manner similar to the results found at the Ott/Story site.

(5) Air stripping - Batch air stripping was evaluated by aerating wastewater for up to 24 hours.

RESULTS

Batch Adsorption Isotherms

Results of adsorption isotherm studies are presented in Figure 33 and Table 27. The activated carbons effected better TOC removal than did the resins. This is similar to the results obtained at the Ott/Story site. The three carbons performed similarly. Of the resins considered, the XE-347 resin produced noticeably better results than the others.

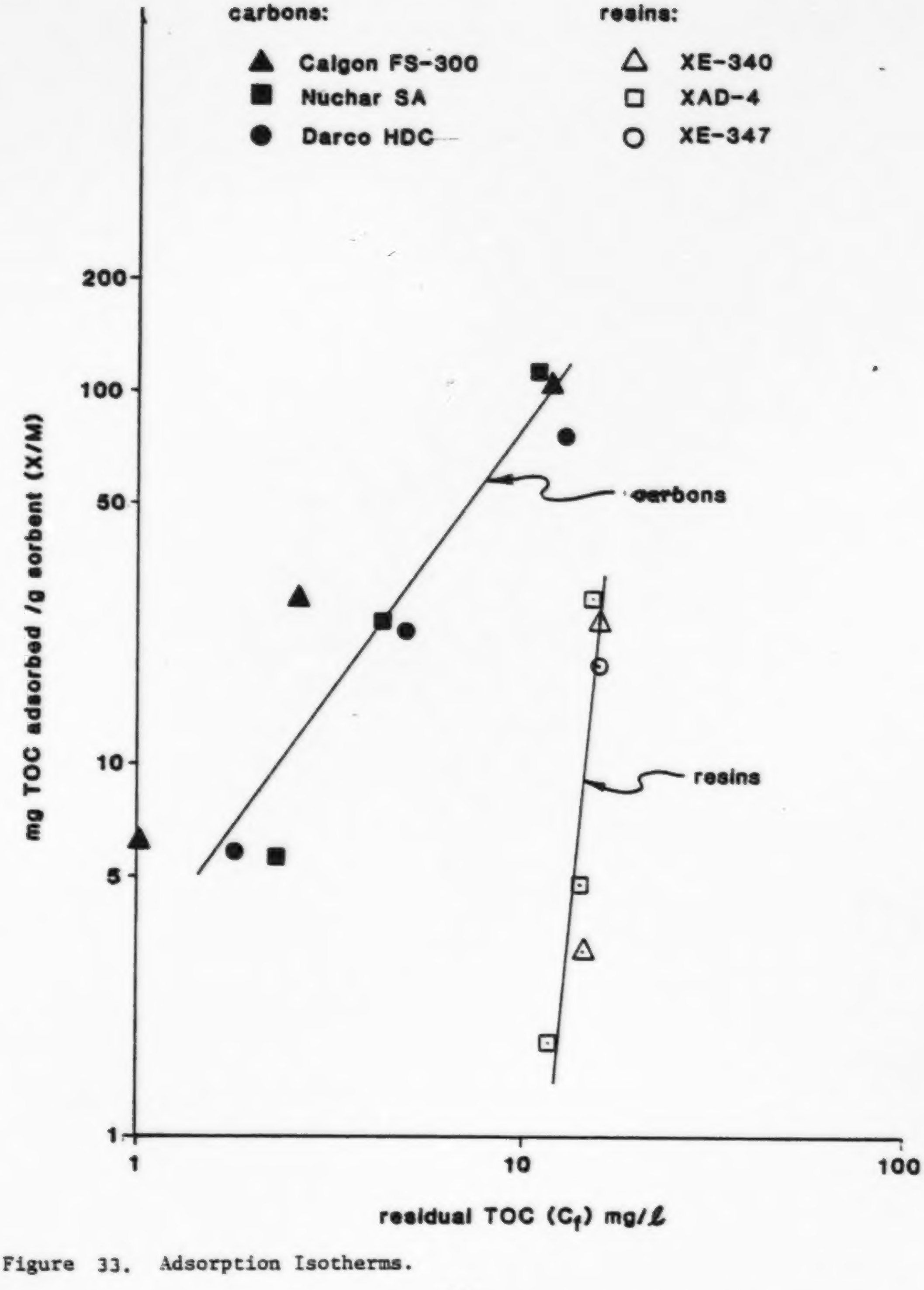

Figure 33. Adsorption Isotherms.

TABLE 27. ISOTHERMS AT PREVAILING pH (7.95) - MARSHALL LANDFILL

Conditions: T = 22°C
initial TOC = 168 mg/l

Sorbent	Dose (mg/l)	Equilibrium TOC (mg/l)	mg TOC sorbed/g of sorbent
Carbons			
Calgon FS-300	0.5	113	102
	5.0	26	28
	25.0	10	6.2
Nuchar SA	0.5	108	112
	5.0	43	24
	25.0	23	5.6
Darco HDC	0.5	126	76
	5.0	49	23
	25.0	18	5.8
Resins			
XE-347	0.5	155	18
	5.0	43	4.2
XE-340	0.5	152	24
	5.0	148	3.2
	25.0	145	0.76
XAD-4	0.5	150	28
	5.0	140	4.8
	25.0	119	1.8
Blank	-	164	-

Activated Sludge Treatment

Although nutrient levels, pH, dissolved oxygen concentration, and heavy metal concentrations were determined to be within acceptable ranges for aerobic biological treatment, attempts at activated sludge acclimation to raw groundwater were unsuccessful as measured by TOC removal and biological solids growth. Influent and effluent TOC averaged about 93 mg/l and attempts at maintaining sludge solids by frequent reseeding were unsuccessful.

Continuous Flow Carbon Adsorption

Based upon adsorption isotherms, continuous flow systems using FS-300 granular activated carbon (GAC) were further evaluated. Operating conditions for systems with two and three columns in series are outlined below:

	2-Column System	3-Column System
Column Diameter, cm (in)	1.90 (0.75)	
GAC Contents, g	Column 1 - 87	Column 1 - 90.5
	Column 2 - 80	Column 2 - 93
		Column 3 - 85
Contact Time, min.	Column 1 - 6.7	Column 1 - 18.1
	Column 2 - 6.2	Column 2 - 36.7
		Column 3 - 53.7
Hydraulic loading rate $l/m^2/sec$ (gpm/ft^2)	1.54 (2.24)	0.59 (0.86)
Bed Volume, ml	Column 1 - 174	Column 1 - 181
	Column 2 - 160	Column 2 - 186
		Column 3 - 170

Influent TOC during these studies ranged from 126 to 182 mg/l.

For the 2-column system, results are presented in Table 28 and Figures 34 and 35. At a system empty bed contact time (EBCT) of about 13 minutes, 91 percent TOC removal was achieved initially; however, after processing about 50 bed volumes (BV), removal had decreased to 70 percent. Effluent TOC was about 40 mg/l.

Results for the 3-column system are presented on Figures 36 and 37; a comparison with the 2-column system is shown in Figure 35. These data indicate slightly better performance at the increased contact time. During

TABLE 28. GRANULATED ACTIVATED CARBON PERFORMANCE - TWO COLUMN SYSTEM (MARSHALL LANDFILL SEEPAGE)

				Column 1				Total System Column 1 and 2			
Cumulative Operating (Min)	Cumulative Flow	Influent TOC	Cumulative TOC Loading	Effluent TOC (mg/l)	TOC Removal %	TOC adsorbed (mg TOC/g carbon)	Bed Volumes Processed	Effluent TOC (mg/l)	TOC Removal %	TOC adsorbed (mg TOC/g carbon)	Bed Volumes Processed
15	.39	137	53	21	85	.6	2.2	12	91	.3	1.2
30	.78	137	106	23	83	1.2	4.5	18	87	.6	2.3
60	1.56	137	212	25	82	2.4	8.9	19	86	1.3	4.7
120	3.12	137	425	36	74	4.9	17.8	24	82	2.5	9.3
180	4.68	137	638	43	69	7.3	26.7	26	81	3.8	14.0
240	6.24	137	851	47	66	9.8	35.7	29	79	5.1	18.7
300	7.8	137	1064	53	61	12.2	44.6	28	80	6.4	23.4
360	9.36	137	1277	52	62	14.7	53.5	31	77	7.6	28.0
420	10.92	137	1490	55	60	17.1	62.4	32	77	8.9	32.7
480	12.48	126	1647	59	53	19.4	71.4	30	76	10.1	37.4
540	14.04	126	1884	65	48	21.7	80.3	32	75	11.3	42.0
600	15.6	126	2081	69	45	23.9	89.2	35	74	12.5	46.7
660	17.16	126	2278	69	45	26.2	98.1	38	70	13.6	51.4
720	18.72	126	2475	69	45	28.4	107.0				

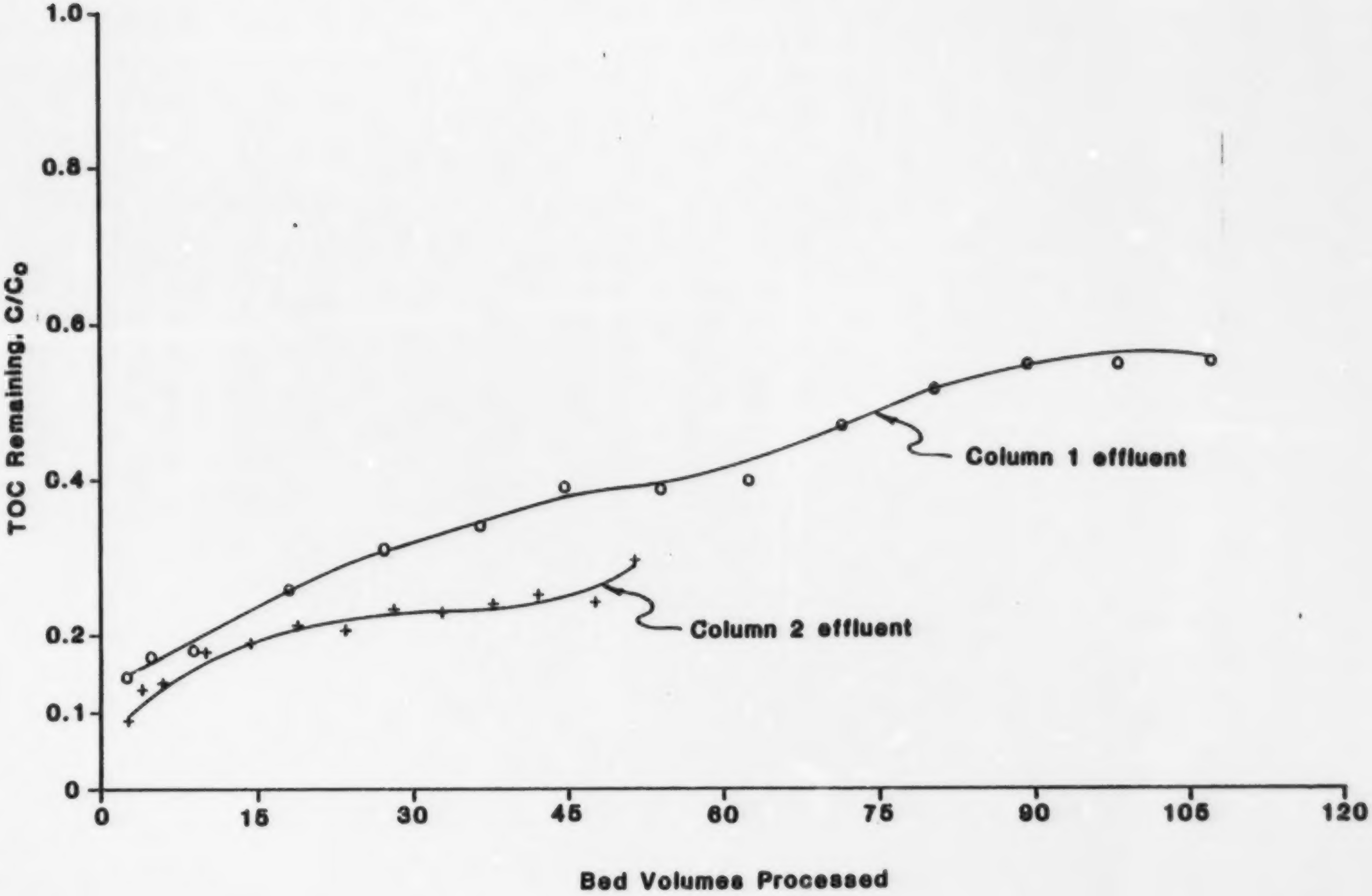

Figure 34. Breakthrough Curve - 2 Column GAC System.

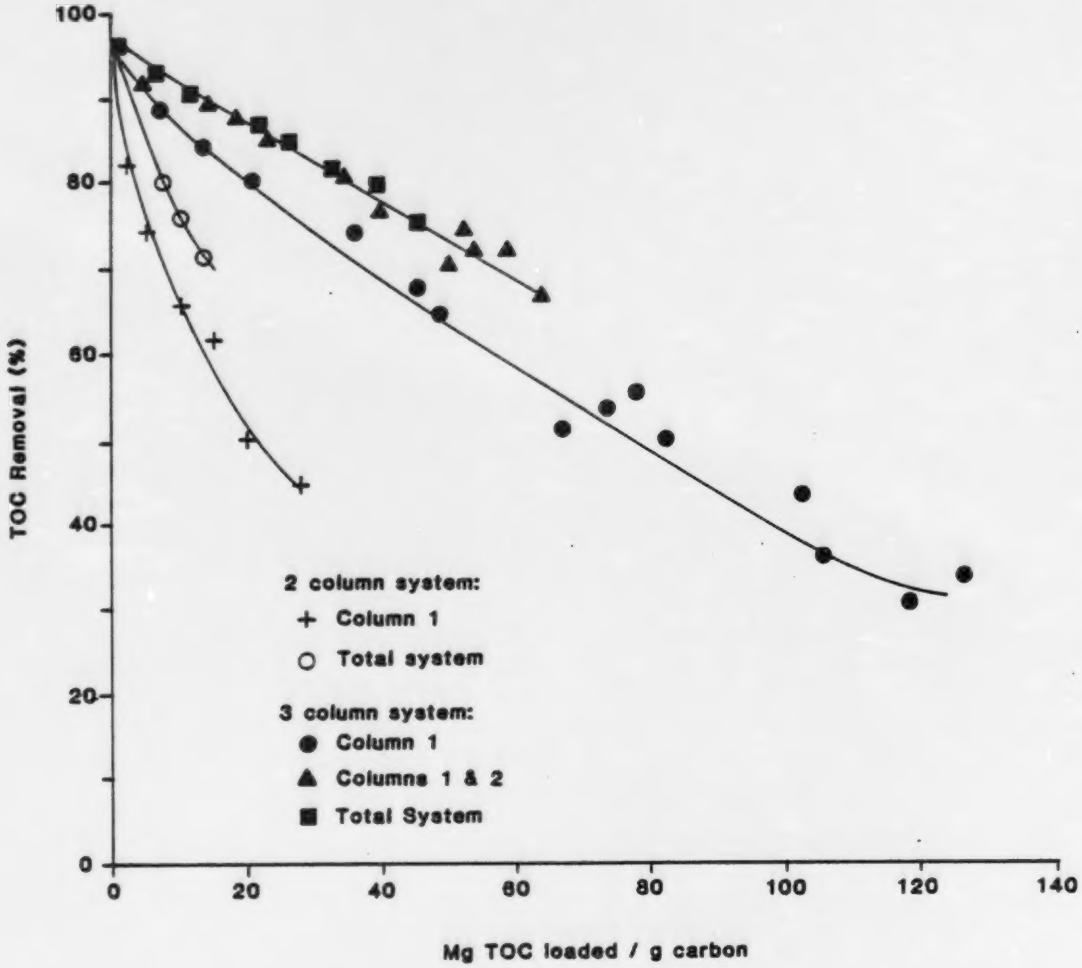

Figure 35. GAC Performance-2 and 3 Column Systems.

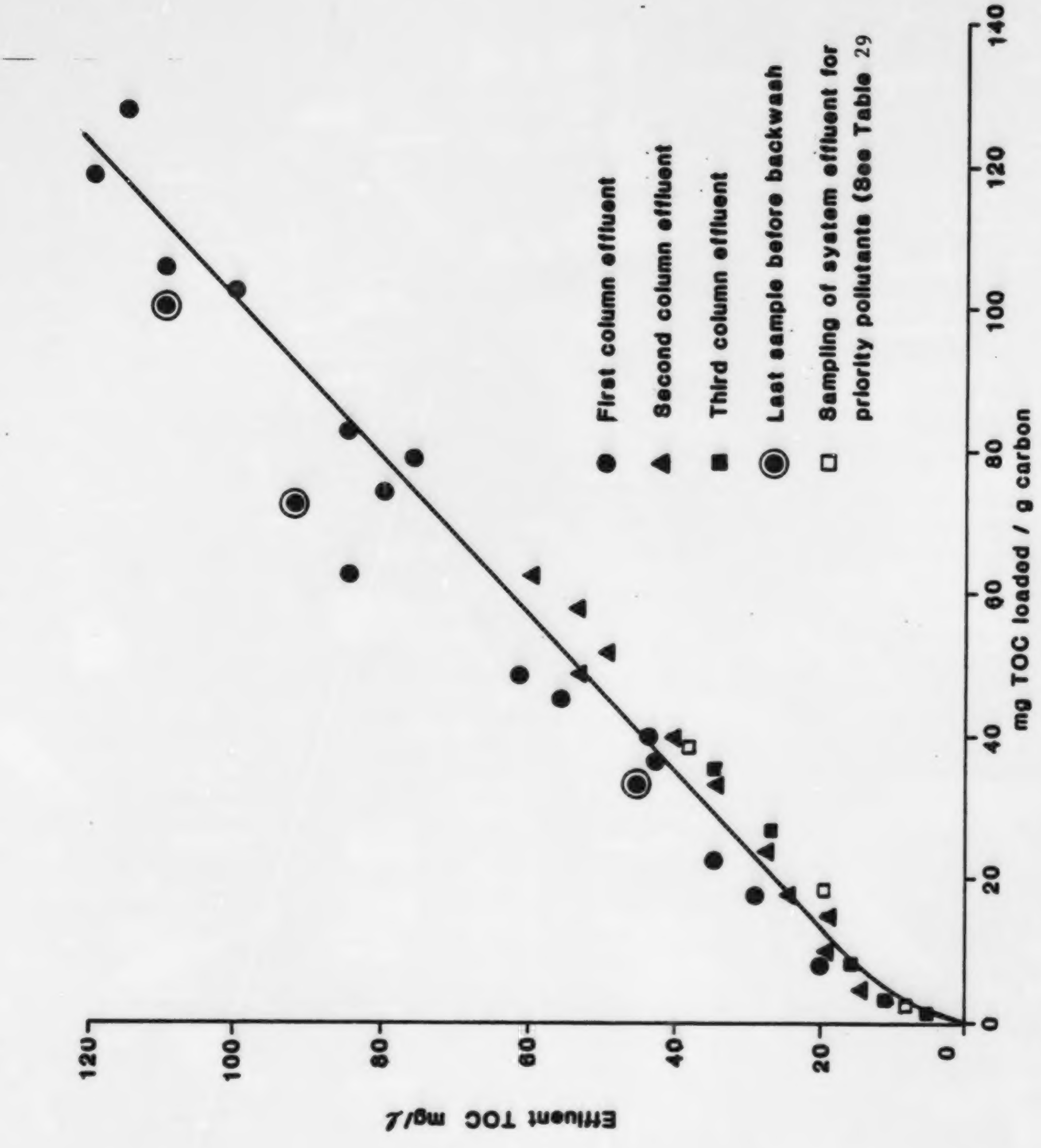

Figure 36. GAC Performance- 3 Column System.

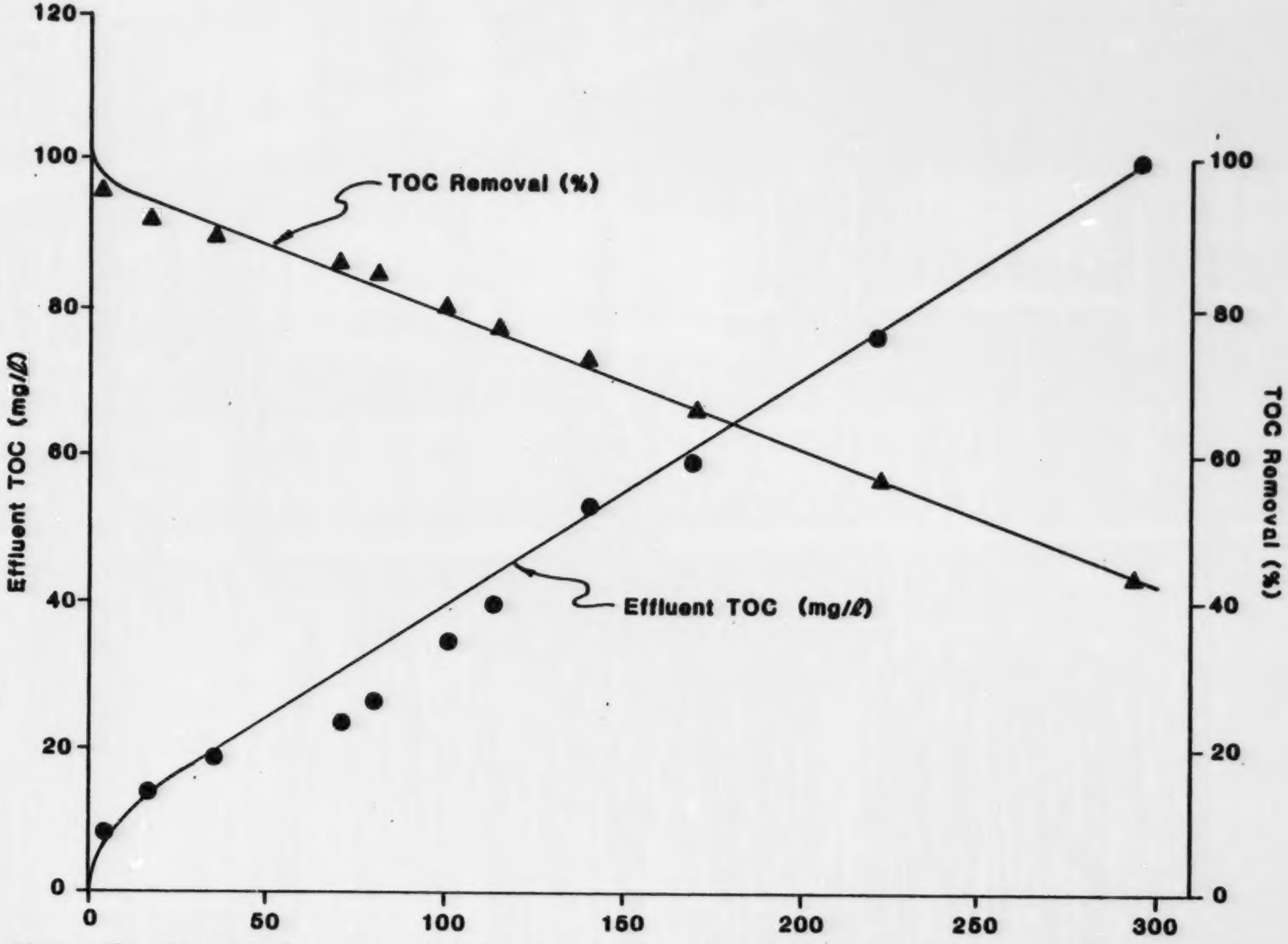

Figure 37. TOC Removal vs. Seepage Volume Processed - 3 Column GAC System.

operation of the 3-column system, the lead column frequently plugged with silt present in the seepage. When this column was backwashed, temporary improvement in TOC removal was observed (see Figure 36).

To evaluate removal of organic priority pollutants, samples of raw seepage and effluent from the 3-column system were obtained at three points on the operating curve as shown on Figure 36. These points correspond to TOC breakthroughs of about 5%, 10%, and 22%. Priority pollutant and TOC results are summarized in Table 29. Priority pollutants detected in the raw seepage but not detected in the carbon column effluents were: benzene, 1,2-dichloropropane, ethylbenzene, tetracholorethylene, toluene, diethyl phthalate. Compounds detected in at least one effluent sample but in not the raw seepage were: 3,3-dichlorobenzidene, anthracene, bis(2-chloroisopropyl)ether, di-n-octyl phthalate, phenanthrene, isophorone. Other pollutants were partially sorbed but were detected in at least one effluent sample. No trend of increasing priority pollutant breakthrough with increased TOC breakthrough is apparent.

To illustrate observed variations in GAC system performance, results of evaluations using Marshall Landfill seepage and groundwater from the Ott/Story site are compared on Figure 38. At comparable TOC loading rates and operating conditions, TOC adsorption per unit weight of GAC was approximately two times greater for the Marshall Landfill seepage than for the Ott/Story site.

Granular Activated Carbon and Activated Sludge Process Train

During the two-month duration of study, a process train consisting of GAC adsorption followed by activated sludge treatment reduced TOC levels to 20 mg/l. However, the GAC column alone reduced the TOC to 23 mg/l, showing that the activated sludge process did not contribute appreciably to TOC removal.

Air Stripping

As indicated by the data summarized below, air stripping (via batch aeration) achieved minimal TOC removal.

Aeration Time (Hr.)	TOC (mg/l)	TOC Removal (%)
0	137	-
6	120	12
24	126	8

This result was not unexpected since, as can be seen from inspection of Table 29, Marshall Landfill leachate did not contain high concentrations of volatile priority pollutants but rather contained primarily phenolics, aromatics, and heavier priority pollutants with low vapor pressures.

TABLE 29. TOC AND PRIORITY POLLUTANT ANALYSES FOR THREE-COLUMN GAC SYSTEM (a)
(MARSHALL LANDFILL SEEPAGE)

Parameter	Raw Seepage	GAC System Effluent (b) Sample 1	 Sample 2	 Sample 3
TOC (mg/l)	175	7-12	19-20	39-43
benzene	1			
chloroform	5	1		
1,2-dichloropropane	1			
ethylbenzene	2			
methylene chloride	8	3	2	6
tetrachloroethylene	1			
toluene	2			
4-nitrophenol	17		11	3
p-chloro-m-cresol	3		2	
bis (2-ethylhexyl) phthalate	16	16		4
diethyl phthalate	2		1	1
di-n-butyl phthalate	2			
3,3'-dichlorobenzidene		4		
anthracene			1	
bis (2-chlorobenzidene) ether			11	3
di-n-octyl phthalate			3	
phenanthrene			<1	
isophorone		5		

(NOTE: Absence of data indicates that the parameter was not detected at the detection limits employed.)

(a) Concentrations are μg/l except where noted

(b) Samples were obtained three times during system operation as follows (See Figure 36):

Sample 1 - over the duration when 1 to 3 mg TOC were loaded per g of carbon

Sample 2 - over the duration when 15 to 17 mg TOC were loaded per g of carbon

Sample 3 - over the duration when 41 to 42 mg TOC were loaded per g of carbon

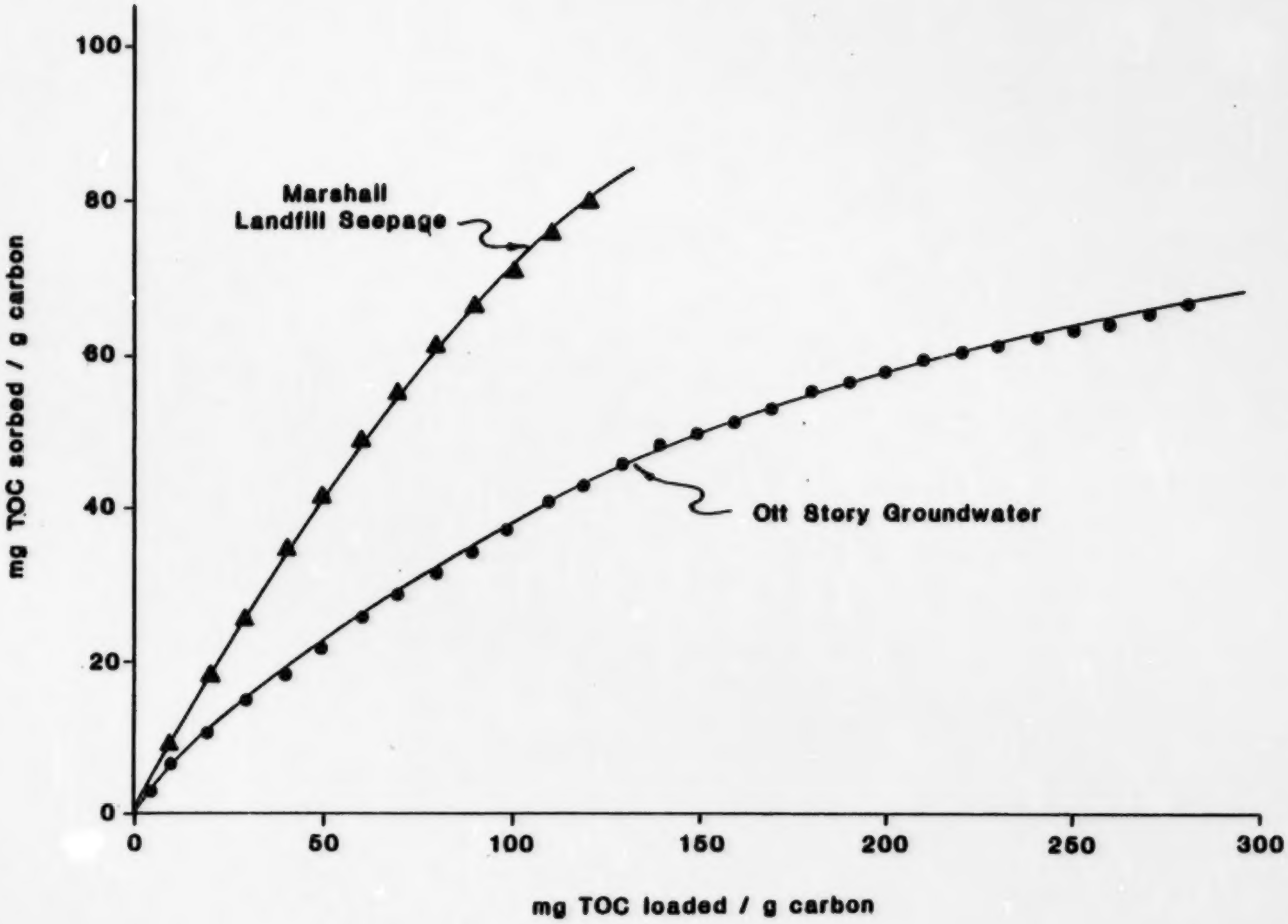

Figure 38. GAC Performance Comparison.

SECTION 7

STUDIES USING GROUNDWATER FROM THE OLEAN WELLFIELD

BACKGROUND

In late 1981, three wells providing 70 percent of the drinking water supply for the City of Olean, New York were found to contain 120 to 250 µg/l of trichloroethylene (TCE). Subsequent testing at other private wells in the area detected TCE at concentrations of 2,000 to 9,000 µg/l. As a result, the city had to revert to using its 60-year old filtration plant to treat an alternate surface water supply source. To aid those relying on private wells, small scale activated carbon adsorption systems were installed at some private homes with individual wells; their performance was monitored by the city and county. Local officials requested and received Superfund status for the site to aid problem investigation efforts and the installation, monitoring, and maintenance of the individual carbon treatment systems. Because of the nationwide prevalence of TCE contamination of drinking water supplies, groundwater from the Olean Wellfield was selected as the fourth contaminant stream to be used to evaluate treatment technologies.

PROCEDURES

Samples from Olean well 37M were collected by municipal personnel. These samples were placed in six completely full one-half gallon glass containers, and shipped overnight to the Baker/TSA laboratory in Beaver, Pennsylvania. Analyses indicated that the groundwater had a COD of 4.8 mg/l and a TCE concentration of 46 µg/l, well below the anticipated concentration of 200-250 µg/l. It was speculated that, because this well had not been used for some time, the configuration of the TCE contamination plume may have changed from that found during earlier problem assessments. Using these samples, batch air stripping tests and adsorption isotherm studies were conducted at the Baker/TSA laboratory. A second set of samples was later obtained from the combined flow of city wells 37M and 38 M by City of Olean personnel under the supervision of the Cattaragus County Health Department. These samples were placed in VOA vials, two of which were air-shipped to the Baker/TSA laboratory and were subsequently found to contain 90 and 95 µg/l of TCE.

Based upon this analysis and results of the air stripping and adsorption isotherm studies, it was determined that approximately 250 gallons of groundwater would be required to develop a granular activated carbon (GAC) breakthrough curve for TCE using a bench scale system. Arrangements then were made to obtain the required quantity of groundwater. The sample was collected from a sample line (with a flow of 1-5 gpm) tapped into a main line served by wells

37M and 38M (main line flow was 1,400 gpm). The sample line was used to fill five 55 gallon steel drums; once filled to overflowing they were tightly sealed and shipped overnight to the Baker/TSA laboratory. Sample collection encompassed approximately 3.5 hr.; cumulative flow through the main line was 302,000 gallons. Analysis of the contents of the fifth drum collected indicated a TCE concentration of 117 μg/l. The sealed, steel drums were stored at ambient temperature at the laboratory until used.

Isotherm studies were repeated with this batch of sample. Continuous flow GAC column studies then were conducted. Study conditions are described below.

During the course of this study, the U.S. EPA Office of Drinking Water conducted a pilot test of air stripping at Olean. Data from the pilot tests were used to calibrate an EPA developed mathematical model for estimating design parameters and treatment costs for volatile organic compound removal by packed column air stripping. A brief description of the EPA model as well as field test results are contained in Appendix A.

RESULTS

Adsorption Isotherm Studies

Adsorption isotherms were prepared for Westvaco Nuchar and Calgon Filtrasorb 300 carbons, and Rohm and Haas carbonaceous resin XE-340. Samples were contacted with the sorbent for two hours at 20°C using a platform shaker operated at 180 excursions/minute. Sorbent doses were 0, 4, 20, 40, 120 and 200 mg/l. At the end of the contact period, samples were filtered and placed in VOA vials.

Figure 39, which compares Olean isotherm data with a single constituent TCE sorption isotherm reported by EPA (7), shows good agreement between the results (EPA also used Filtrasorb 300). The Nuchar carbon, a powered carbon, exhibited somewhat poorer TCE absorption characteristics. Resin sorption data do not show a clear trend and are not plotted. Since there were indications that the manufacturer planned to discontinue this product, additional work with resins was not undertaken.

Continuous Flow Carbon Adsorption

Continuous flow granular activated carbon (GAC) column studies were conducted using two columns in series; however, to facilitate observation of TCE breakthrough the first column was divided into three segments. Operating data for the columns are given below:

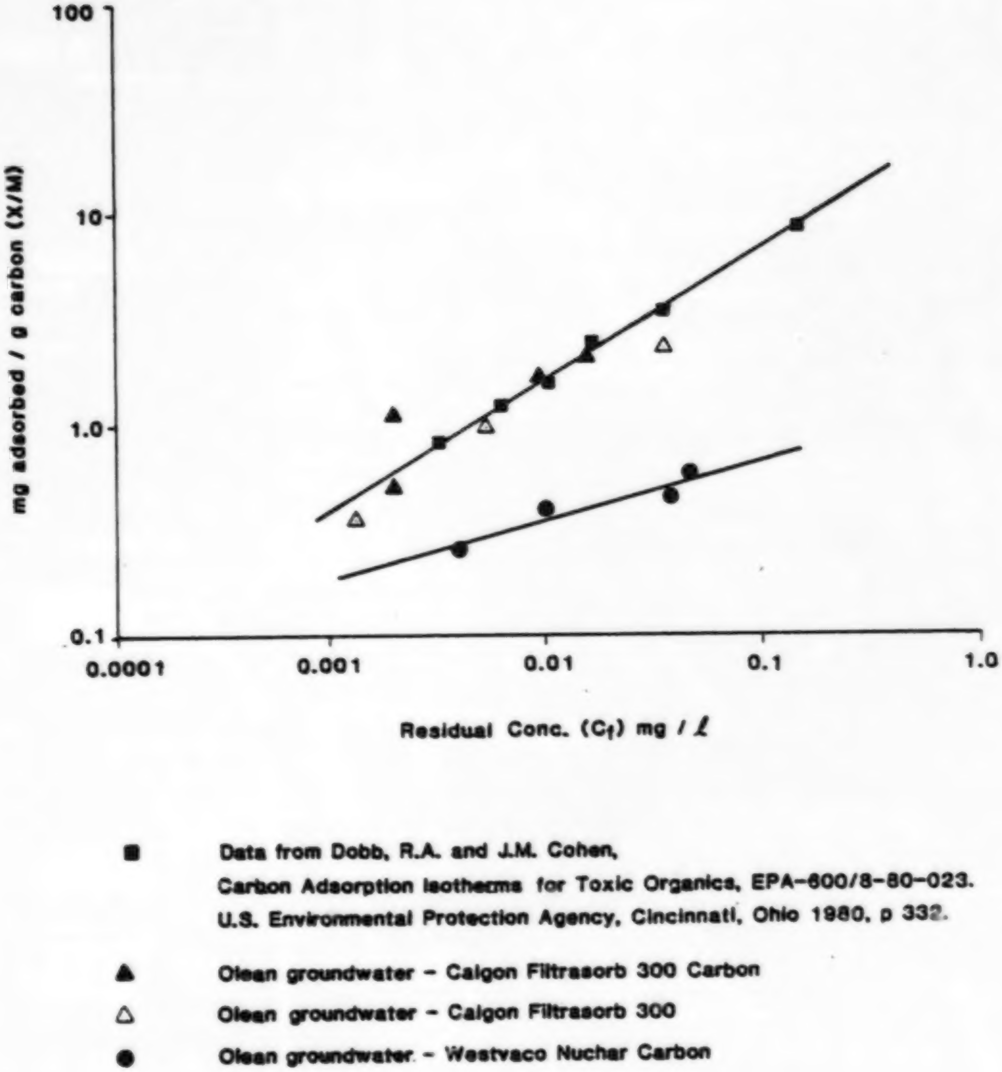

Figure 39. TCE Adsorption Isotherms.

Column	Cumulative Carbon Volume (cm^3)	Average Cumulative EBCT (min.)	Total Bed Volumes Processed	Effluent TCE
1A	123.8	3.1	6907	ND
1B	255.8	6.4	3343	ND
1C	387.7	9.7	2206	ND
2	793.1	19.8	1078	ND

(ND - not detected)

This system was operated until the supply of contaminated well water was exhausted. No TCE breakthrough was detected at that time. However, summarized below is the theoretical TCE breakthrough calculated on the basis of published Freundlich isotherm parameters for a constant TCE concentration of 100 µg/l:

Bed Volumes Processed	Effluent TCE Concentration (µg/l)
2000	1
5000	5
7750	10

This suggests that some breakthrough should have been detected during the experimental study. It was observed that volatilization losses of TCE from the storage containers prior to and during use reduced the actual influent TCE concentration below 100 µg/l. Monitoring of these containers indicated that TCE losses ranged up to 51% with the average loss being 34% (27 µg/l). These monitoring results were used to calculate the actual TCE load applied to the carbon. The loading on Column 1A at termination of the run was calculated to be 0.762 mg TCE/g carbon. This should have resulted in a theoretical effluent TCE concentration of 3 µg/l. The measured value was <1µg/l.

Total plate counts (48 hours) were made of carbon effluent to investigate the possibility of biological growth in the GAC columns and subsequent contamination of the treated water. The following samples were assayed:

GAC column influent during the processing of BV 2556-3803	≅500 colonies/1 ml
Column 1A effluent after 2556 BV	≅7,000 colonies/1 ml
Column 1A effluent after 3,456 BV	≅10,000 colonies/1 ml

These data indicate elevated plate counts following GAC treatment. This may partially explain the non-detectable TCE levels in the carbon effluent. Further study in this area for health effect determination may be warranted when carbon adsorption systems are planned for the treatment of residential or small scale water supplies.

EPA Modeling of Packed Air Stripping

The Olean site was an ideal situation for evaluation of advanced TCE removal techniques. During the course of Baker/TSA studies at this site, the State of New York Department of Health requested further EPA research involvement resulting in a field evaluation of TCE removal by packed column air stripping. Operation of the field pilot system and development of a mathematical model for the system was carried out by the EPA Office of Drinking Water - Technical Support Division.

Appendix A contains a reproduced report describing the EPA field work and evaluation. Their results show that greater than 99 percent TCE can be removed by air stripping economically.

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APPENDIX A

PACKED COLUMN AIR STRIPPING PILOT TEST
OLEAN, NY - MAY 25, 1982

The United States Environmental Protection Agency (EPA), Office of Drinking Water (ODW), Technical Support Division (TSD) is conducting a program for evaluation of packed column air stripping for removal of volatile compounds from contaminated water supplies. TSD has constructed a portable pilot packed column air stripping system which is used to generate data for field evaluation of the treatment process. This report discusses one in a series of pilot packed column air stripping field tests. This field test was conducted May 25, 1982, at Olean, NY. The contaminant monitored was trichloroethylene in levels ranging from 170 to 210 µg/1. The packing material evaluated was 5 cm (2 in.) plastic saddles.

In November 1981 a portion of the City of Olean's water supply was found to be contaminated with trichloroethylene. Subsequent analyses revealed that three of Olean's four municipal wells were contaminated with trichloroethylene in excess of 100 µg/1. These three wells, which supplied 70% of the City's water supply, were shut down and a 60-year old filtration plant was returned to service. The City is investigating the source of the contamination and possible treatment alternatives. The TSD pilot system was used to evaluate the treatment alternative of packed column air stripping.

The TSD pilot packed column air stripping system (shown in Figure A-1) consists of a 0.6 m (2 ft.) diameter aluminum column packed with 5.5 m (18 ft.) of 5 cm (2 in.) plastic saddles. Eighteen sample ports were installed at 0.3 m (1 ft.) intervals along the column height to sample the center 0.3 m (1 ft.) of the column. This sampling system allowed monitoring the concentration profile of trichloroethylene along the column height. The column was designed to operate at air to water volume ratios of 10, 15, 25, 50, 75, and 150.

The field evaluation at Olean consisted of operation at the 6 air to water ratios shown in Table A-1. At Olean, 20 samples (including influent and effluent) were collected at each air to water ratio for a total of 120 samples. Fifty-six of these samples were analyzed by the liquid-liquid extraction GC technique for trichloroethylene. These data were plotted, as shown in Figure A-2, as concentration vs length of travel through the packed column. From Figure A-2 it was observed that an effluent concentration of less than 1 µg/1 could be obtained despite the high influent concentration of 200 µg/1. From Figure A-2 it was observed that the concentration declined, as expected, as the water passed through the packed column. It was also apparent that increasing the air to water ratio improved the removal efficiency.

Not so apparent in Figure A-2 was the phenomena that at high air to water ratios the concentration profile was linear; whereas, at low air to water ratios the concentration profile was curvilinear. A transition from linear to curvilinear was observed from the high to the low air to water ratio. This curvature was due to the air becoming saturated with trichloroethylene in the lower sections of the stripping column. When this happened, the packed column was unable to effectively remove trichloroethylene from the water phase. This condition was forced in the pilot system so that Henry's coefficient for trichloroethylene could be determined in the field conditions experienced at Olean.

A data analysis procedure has been developed to determine Henry's coefficient, the mass transfer coefficient, and the influent concentration from the concentration profiles shown in Figure A-2. The procedure consists of estimating the above three parameters by fitting a concentration profile math model to the data points using a non-linear multi-regression analysis. Equal statistical weight is allowed for each data point. The math model is shown below and plotted along with the data points in Figure A-2. The relative standard deviation between the model and all the data points was 6%.

Concentration Profile Math Model:

$$X_Z = X_T * \frac{(R*A) - 1}{(R*B) - 1}$$

Where: $$A = \exp Z* \frac{K_{La}}{L} * \frac{(R - 1)}{R}$$

$$B = \exp Z_T* \frac{K_{La}}{L} * \frac{(R - 1)}{R}$$

$$R = \frac{G''}{L''} * \frac{H}{P_t} = \frac{(G*pa/MWa)}{(L*pw/MWw)} * \frac{H}{P_t}$$

Where: G = Air loading ($m^3\ m^{-2}\ sec^{-1}$)

L = Liquid loading ($m^3\ m^{-2}\ sec^{-1}$)

pa = Density of air ($Kg\ m^{-3}$)

pw = Density of water ($Kg\ m^{-3}$)

MWa = Molecular weight of air ($28.8\ Kg\ KM^{-1}$)

MWw = Molecular weight of water ($18.0\ Kg\ KM^{-1}$)

Z_T = Packing height (m)

Z = Location within column measured from bottom of column (m)

K_{La} = Mass transfer coefficient (sec^{-1})

X_T = Influent concentration ($\mu g\ l^{-1}$)

X_Z = Concentration at location Z ($\mu g\ l^{-1}$)

R = Stripping Factor

G" = Air molar loading ($KM\ m^{-2}\ sec^{-1}$)

L" = Liquid molar loading ($KM\ m^{-2}\ sec^{-1}$)

H = Henry's coefficient (atm KM H_2O KM^{-1} air)

P_t = Operating pressure (1 atm)

The Henry's coefficient was estimated as that value which results in the minimum relative standard deviation between the concentration profile math model and the data points, determined by an iteration procedure. The relative standard deviation (RSD) was computed as follows.

$$RSD = \sqrt{\frac{\sum_{i=1}^{N}\left(\frac{Xi - X_Z}{X_Z}\right)^2}{N}}$$

Where: RSD = Relative standard deviation

Xi = Concentration profile data point

X_Z = Concentration profile math model

N = Number of data points

This relationship is shown in Figure A-3 for the 10:1 air to water ratio. Throughout Figure A-3 the influent concentration and mass transfer coefficients were determined by a regression analysis. This relationship revealed that a minimum relative standard deviation occurred at 3.4%. This minimum relative standard deviation indicated that the estimated value for Henry's coefficient was 175 atm KM H_2O KM^{-1} air (0.13 atm m^3 H_2Om^{-3} air).

The mass transfer coefficients for each air to water ratio were determined by a method similar to that used in determining Henry's coefficient. The relationship between the relative standard deviation and each mass transfer coefficient are shown in Figure A-4. In Figure A-4 the influent concentration was optimized throughout while the Henry's coefficient was held constant at 175 atm. Similar to Figure A-3, the minimum points indicated the best fit values for the mass transfer coefficients. The best fit values for the mass transfer coefficients are included in Table A-1.

From Figure A-4 it was observed that a trend existed between the best fit value for the mass transfer coefficient and the air to water ratios. For volatile compounds, such as trichloroethylene, this trend is generally believed to be due to the liquid loading. One of the key parameters in designing a packed column air stripping system is this relationship between the mass transfer coefficient and the liquid loading. Examination of this data set revealed that the relationship was log-log linear between liquid loadings 0.005 through 0.026 $m^3\ m^{-2}\ sec^{-1}$ (7.3 through 38 gal. $min^{-1}\ ft^{-2}$). Above 0.026 $m^3\ m^{-2}\ sec^{-1}$ liquid loading the relationship was not linear. This was probably due to hydraulically overloading the packed column. This relationship is shown in Figure A-5. A linear regression of the data between liquid loadings 0.005 and 0.026 $m^3\ m^{-2}\ sec^{-1}$ resulted in a correlation coefficient of 0.996 -- an excellent fit. The equation of the best fit line was as follows.

$K_{La} = 0.12*L^{0.59}$ (for 5 cm plastic saddles)

Where: K_{La} = Mass transfer coefficient (sec^{-1})

L = Liquid loading ($m^3\ m^{-2}\ sec^{-1}$)
for $0.005<L<0.026\ m^3\ m^{-2}\ sec^{-1}$

The economics of removing trichloroethylene from the contaminated water supply at Olean, NY, was evaluated using a cost optimized design procedure developed by TSD. The design parameters for the City of Olean, NY, are as follows.

Flow = 0.14 $m^3\ sec^{-1}$ (3.25 MGD)

Temperature = 10.6°C

Interest Rate = 10%

Amortization Time = 20 years

Power Cost = 6¢ KW/hr

Henry's Coefficient = 175 atm KM H_2O KM^{-1} air

Safety Factor for Henry's Coefficient = 1.1

Safety Factor for K_{La} = 1.1 for 5 cm saddles
(1.25 for 2.5 cm saddles)

Safety factors are assigned which are based upon the closeness of fit of the data points to the model. Based on the results of this field work with the appropriate safety factors applied, the packed column size and estimated cost are shown in Table A-2.

Table A-2 presents a series of packed column air stripping systems and cost estimates for trichloroethylene removal efficiencies from 80 to 99%. The packed column systems shown in Table A-2 are based on the K_{La} equation and Henry's coefficient. The cost estimate indicated that 99% trichloroethylene removal can be obtained with a total production cost of 1.9¢ m^3 (7.2¢ per 1,000 gal) using 5 cm (2 in.) plastic saddles.

The packing material investigated in this study was 5 cm (2 in.) plastic saddles. TSD has also investigated at other municipalities trichloroethylene removal using 2.5 cm (1 in.) plastic saddles. The Henry's coefficient of 175 atm observed at Olean, NY, was in excellent agreement with Henry's coefficient observed at these other municipalities. The relationship between the mass transfer coefficient and the liquid loading for 2.5 cm (1 in.) plastic saddles observed at the other municipalities was as follows.

$$K_{La} = 0.094L*^{0.48} \quad \text{(2.5 cm plastic saddles)}$$

Where: K_{La} = Mass transfer coefficient (sec^{-1})

L = Liquid loading ($m^3\ m^{-2}\ sec^{-1}$)
for $0.007<L<0.024$ ($m^3\ m^{-2}\ sec^{-1}$)

This relationship for 2.5 cm (1 in.) plastic saddles observed at other municipalities and the relationship for 5 cm (1 in.) plastic saddles observed at Olean, NY, cannot be directly compared. However, the relationship for 2.5 cm plastic saddles can be used to compare the size and estimated cost of a system using 2.5 cm plastic saddles to that of a system using 5 cm plastic saddles at Olean, NY. Table A-2 also includes a series of packed column air stripping systems using 2.5 cm plastic saddles. The estimated production cost for a 99% TCE removal system is 2.1¢ m^{-3} (7.9¢ per 1,000 gal.). This is 10% higher than the system using 5 cm (2 in.) plastic saddles; however, this may be due to the different safety factors used.

The author expresses special thanks to the employees of Olean's municipal water department in erecting and operating this pilot system. Without their courteous and professional help this field evaluation would not have been possible.

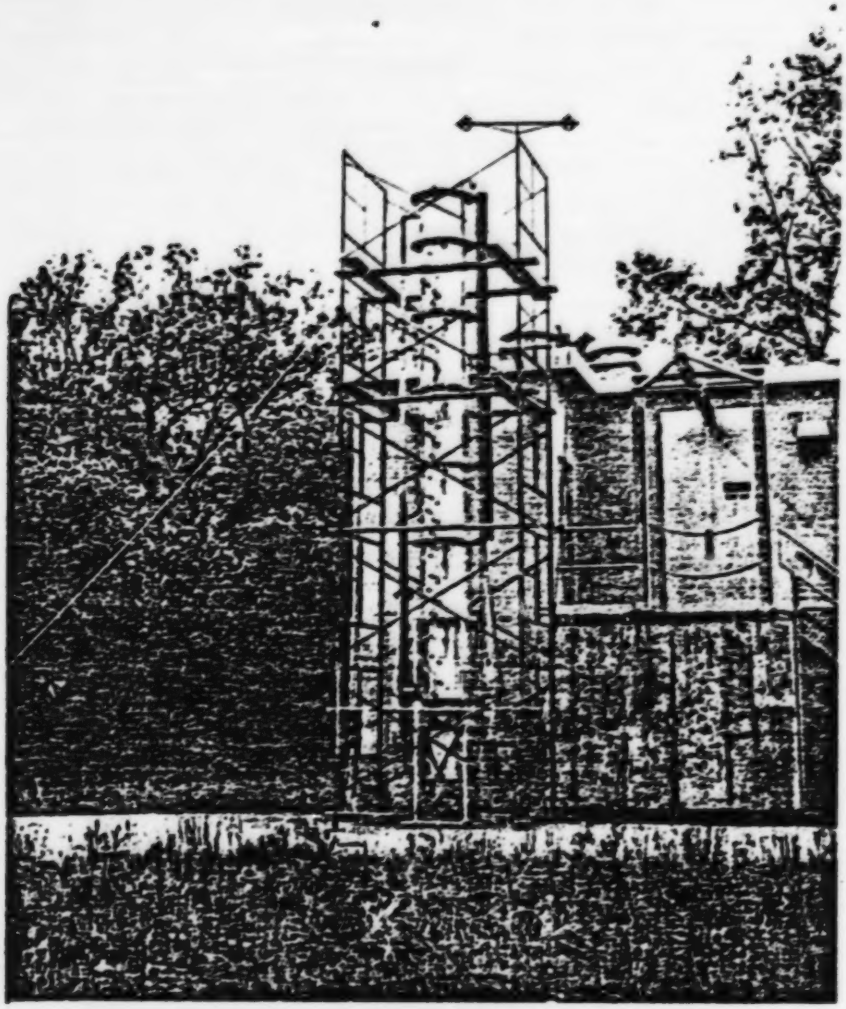

Figure A-1. Packed column air stripping pilot system at Olean, NY on 5/25/82.

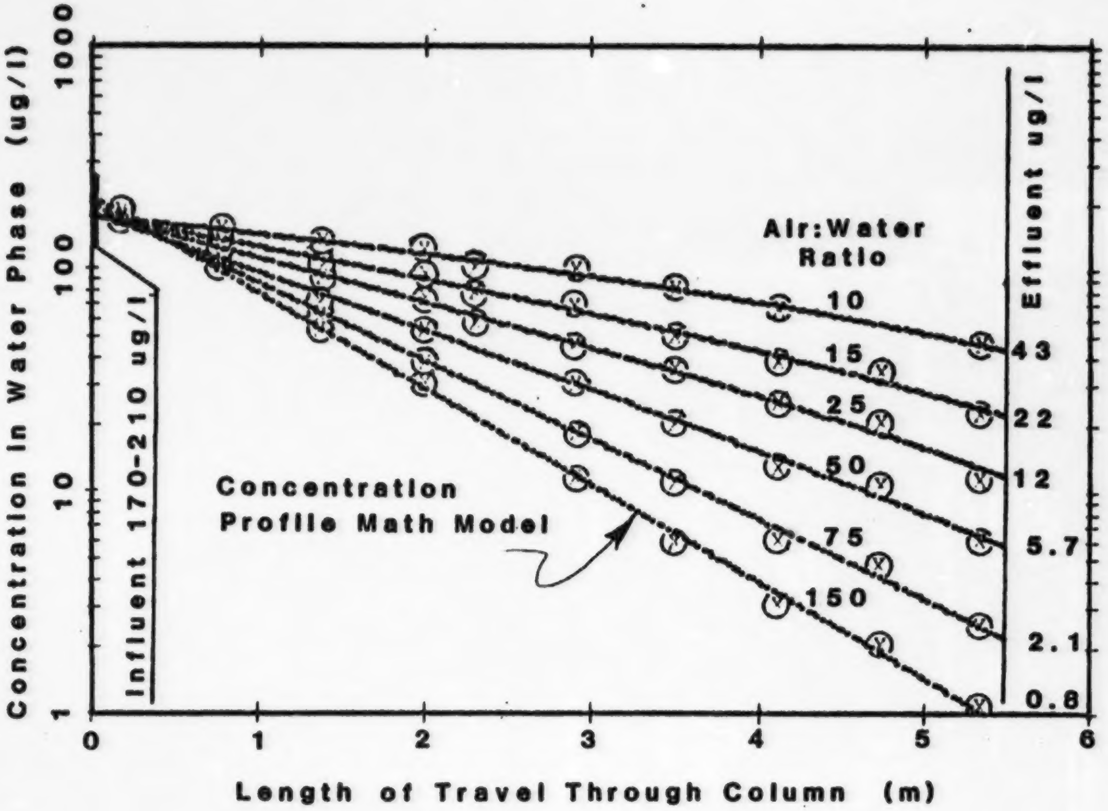

Figure A-2. Trichloroethylene concentration profile at Olean, NY on 5/25/82.

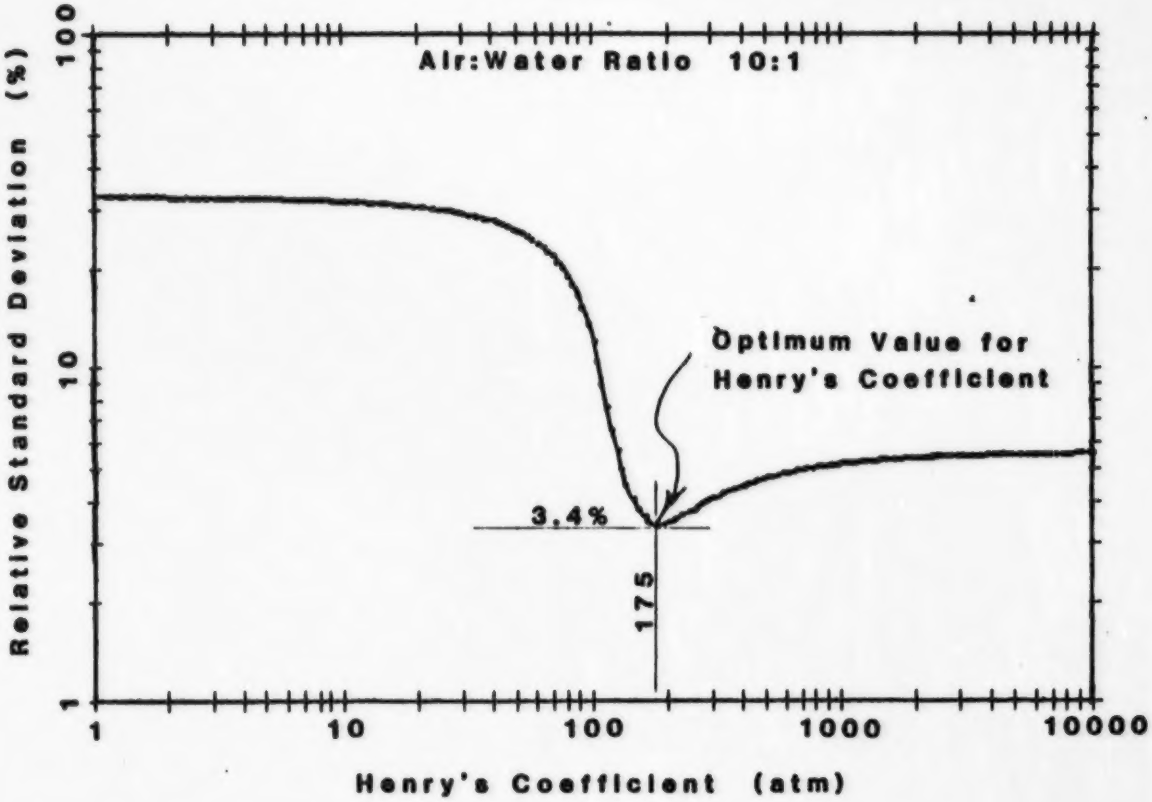

Figure A-3. Relative standard deviation vs. Henry's coefficient for trichloroethylene at Olean, NY on 5/25/82.

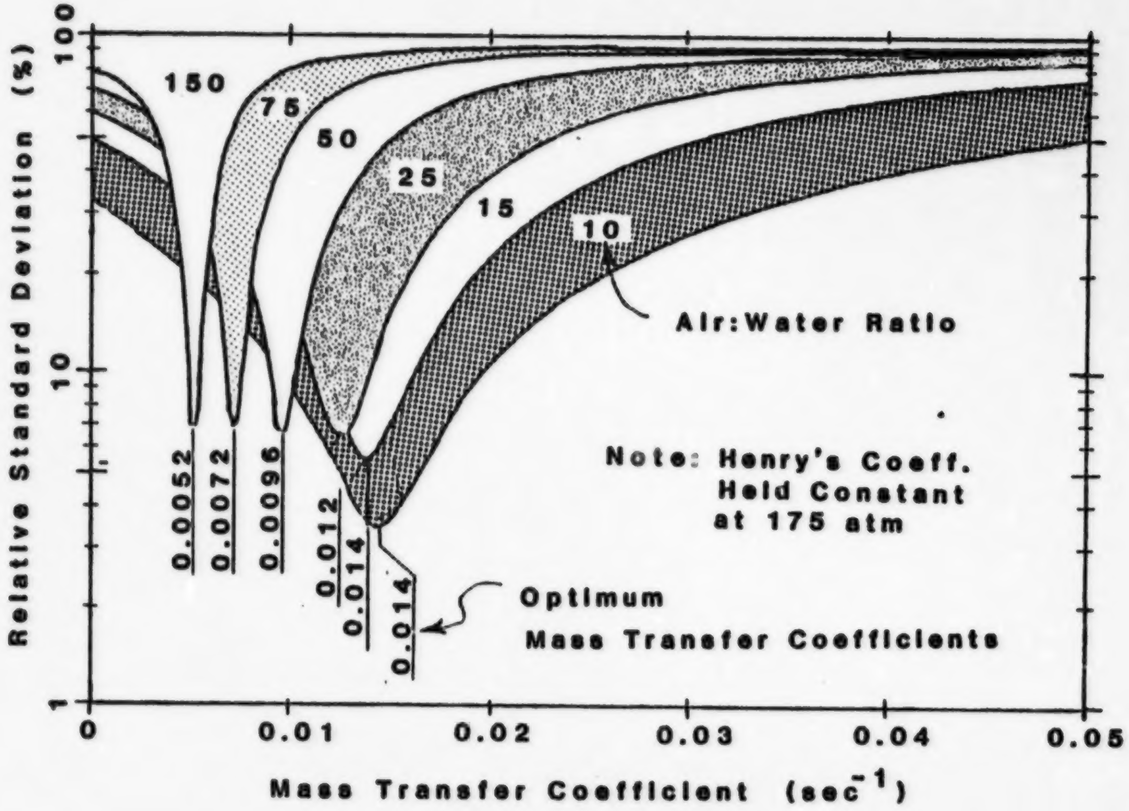

Figure A-4. Relative standard deviation vs. KLa for trichloroethylene at Olean, NY on 5/25/82.

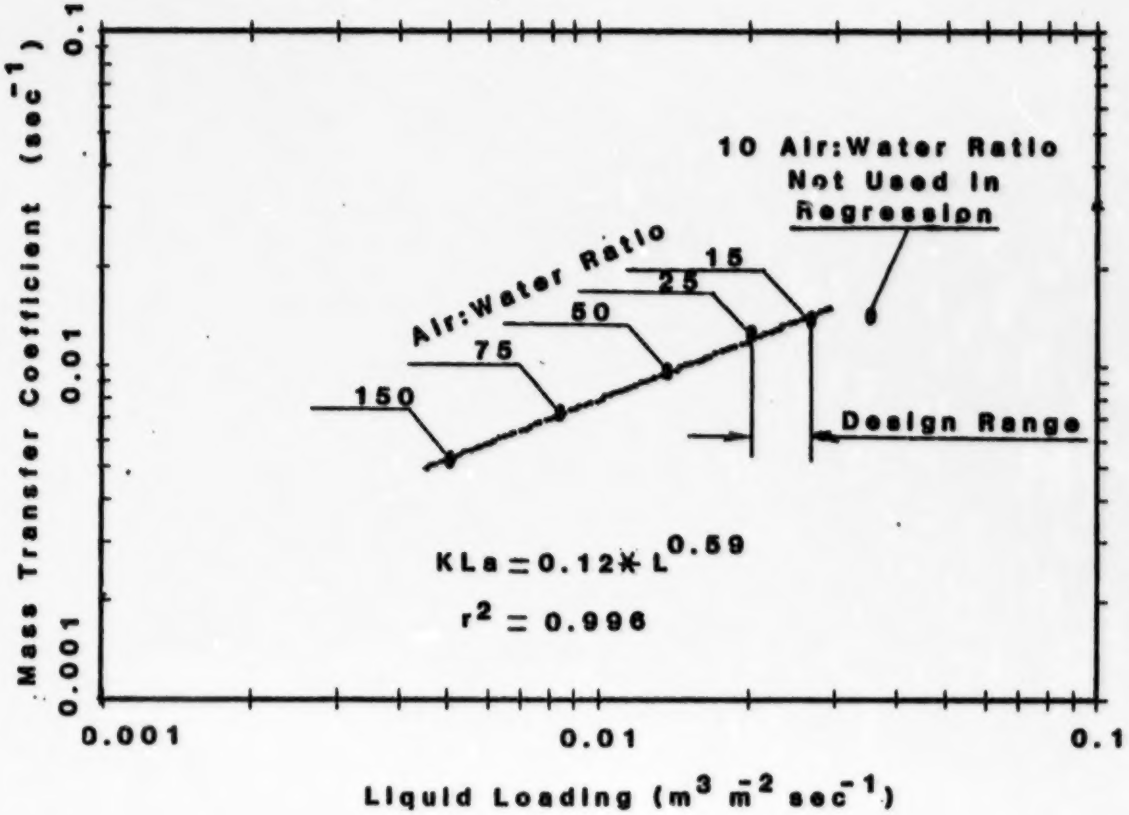

Figure A-5. Mass transfer coefficient vs. liquid loading at Olean NY on 5/25/82 - Trichloroethylene.

TABLE A-1. PILOT PACKED COLUMN AIR STRIPPING RESULTS
OLEAN, NY - MAY 25, 1982

Water Temp. = 10.5°C: Air Temp. = 20°C

	Run					
	1	2	3	4	5	6
Liquid Loading (m^3 m^{-2} sec^{-1})	0.035	0.026	0.020	0.014	0.0082	0.0050
Liquid Loading (GPM ft^{-2})	51	38	29	20	12	7.4
Air Loading (m^3 m^{-2} sec^{-1})	0.34	0.43	0.49	0.66	0.72	0.74
Air Loading (CFM ft^2)	67	85	96	130	140	145
Air:Water Volume Ratio	10	16	24	48	88	150
% Removed*	75	87	93	96.8	98.9	99.6
Mass Transfer Coeff (sec^{-1})*	0.014	0.014	0.012	0.0096	0.0072	0.0052
Influent Concentration (µg/1)*	174	173	175	177	192	207
Effluent Concentration (µg/1)*	44	22	12	5.7	2.1	0.8

*Based on curve fitting 9 or more data points.

TABLE A-2. PACKED COLUMN AIR STRIPPING DESIGNS

		% TCE Removal				
		80	90	95	98	99
5 cm (2 in.) Plastic Saddles						
Packed Column Size						
Number of Columns						
Column Diameter	(ft)	8.8	9.2	9.7	10	10
Packing Height	(ft)	13.6	19.0	23.2	29.7	35.4
Air Flow	(SCFM)	5,500	6,400	7,400	8,000	8,000
Air Pressure Drop	(in H_2O)	2.8	3.2	3.4	3.8	4.2
Economic Estimate						
Total Capital	(K$)	215	245	280	320	350
Operating Cost	(K$/yr)	27	30	35	40	43
Production Cost	(c/1,000 gal)	4.5	5.3	5.7	6.8	7.2
2.5 cm (1 in.) Plastic Saddles						
Packed Column Size						
Number of Columns		1	1	2	2	2
Column Diameter	(ft)	10.0	10.0	8.2	8.8	8.9
Packing Height	(ft)	12.6	18.0	19.0	22.5	25.8
Air Flow	(SCFM)	4,000	4,000	6,400	7,700	8,200
Air Pressure Drop	(in H_2O)	3.0	3.4	3.4	3.6	3.8
Economic Estimate						
Total Capital	(K$)	230	270	350	410	450
Operating Cost	(K$/yr)	26	30	32	36	39
Production Cost	(c/1,000 gal)	4.6	5.4	6.4	7.3	7.9